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REVIEW COPY

ASSESSMENT OF THERMODYNAMIC DATA AND NEEDS, INCLUDING THEIR ECONOMIC IMPACT, FOR DEVELOPMENT OF NEW FOSSIL FUEL REFINING PROCESSES

W. V. Steele, R. D. Chirico, W. B. Collier,
R. H. Harrison, and B. E. Gammon

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National Institute for Petroleum and Energy Research
A Division of IIT Research Institute
P.O. Box 2128
Bartlesville, Oklahoma 74005
918/336-2400

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PREFACE

This report is a state-of-the-art assessment of the thermodynamic data available and data needs for the processing of heavy petroleum, shale oil, tar sands, and coal liquids. It has been produced in partial fulfillment of the plan for thermodynamics research outlined in the NIPER FY86 Annual Research Plan.

The assessment contains two background chapters on Energy Outlook and Future Refinery Needs as an overall introduction to the subject matter. Two chapters on economics follow: one on the previous economic impact of thermodynamics on the petroleum industry and the second on the possible economic impact of thermodynamics on the processing of the alternate crudes.

Chapters 5 through 9 detail the thermodynamic properties needed, their present status and future needs, including some details of compound types and problems to be solved for processing heavy petroleum, shale oil, tar sands, and coal liquids.

After a chapter detailing the interaction between thermodynamics, kinetics, and catalysis, the final two chapters in the assessment are devoted to details of previous assessments of the need for thermodynamic measurements in this general field and a listing of the active laboratories making this type of measurement.

This report does not cover thermodynamic data needs for (a) coal gasification, and (b) enhanced oil recovery (EOR). The former has been the topic of a recent similar report by the Gas Research Institute (GRI). The latter is the research topic of a separate group within NIPER who would be more competent to make a review of data available and future needs for EOR via thermodynamics research.

EXECUTIVE SUMMARY

This report, funded by the Advanced Processing Technology program of the Department of Energy's Office of Fossil Energy, is a survey of the present data base and future data needs for thermodynamic properties of substances related to the future refining of heavy petroleum, shale oil, tar sands, and coal liquids. It examines the past economic effect of accurate and precise thermodynamic data on the efficiency of the petroleum industry and projects the results into the future economic impact of such data on problems in the utilization of the alternate fuels. The report examines the differences which characterize the liquids that will occur in the manufacture of fuels from heavy petroleum, shale oil, tar sands, and coal liquids compared with those that are presently handled by the petroleum industry. It concludes that although a start has been made on obtaining the relevant data base, enough to prove that the new requirements constitute more than a simple extension of the scope and ranges of existing data bases, a sustained, well-founded, well-funded effort is needed to give the industry a firm foundation on which to build the refinery operations of the future.

Sustainment of both economic and military security of the United States requires a solid, well-founded energy policy utilizing all our fuel sources. The light petroleum refining industry is about 95 percent energy efficient, which has led to a continued supply of reasonably priced fuel for industrial requirements. Thermodynamic data on the components of light petroleum was used to predict conditions favorable for carrying out desired chemical conversions, showing where catalyst development would or would not pay, setting the size and strength of units within the plant, and setting energy requirements for running such plants. Continued economic viability requires that such calculations be made on future refining operations and new energy-efficient processes be developed where necessary. Requirements of the refinery of the future can be summarized as follows:

- o There will be no by-products having less value than the crude. Production of residual fuels will discontinue.
- o There will be considerable hydrogenation and heteroatom removal facilities, and the hydrogen required must not come from the desired products.
- o There will be features which will minimize energy requirements.

- o The refinery must also be capable of working with a range of crude feedstocks.

The main problem areas in the processing of heavy petroleum, shale oil, tar sands, and coal liquids are hydrogen requirements, the need to remove large amounts of heteroatoms, the presence of metals, and coke formation reducing yields. Present proposed processes for the production of oil from shale and the liquefaction of coal are energy intensive and uneconomic. This report details the use of thermodynamic data in the design and operation of possible processes to address these problems. The forces that hold the materials within their mineral matrices as well as bind the materials together were not of great concern in the past, but the understanding of physical and chemical methods of disrupting these forces are tantamount to the development of efficient extraction and conversion methods. Thermodynamic data is required to give the necessary fundamental guidance to the selection of methods suitable for extraction and conversion of these materials. Large economic savings can be made with such knowledge. A 20 percent reduction in the hydrogen required for nitrogen removal in a shale oil refining operation of two million barrels per day would result in a \$3 million saving in operating costs. Many proposed processes are run at high temperature where condensation reactions cause the formation of high molecular weight species and exacerbate the problems. There is every reason to believe that mild pretreatment conditions can eliminate formation of undesirable species formed in the more severe conditions proposed at present.

The report examines the range of thermochemical and thermophysical properties needed for efficient design and operation of processes in the extraction and processing of heavy petroleum, shale oil, tar sands, and coal. It outlines the development of key data on pure compounds and selected mixtures to serve as a basis for prediction of the thermodynamic properties of the wide range of substances found in the alternate fuels. Thermochemical property measurements on polycyclic hydrocarbons; heteroatom compounds containing nitrogen, oxygen, and sulfur; partially hydrogenated derivatives of both of the above compound sets; multiheteroatom-containing compounds; and organometallic compounds are reviewed and the need for further measurements outlined. A concerted experimental and theoretical development program of research in thermophysical property measurement is outlined. Among the recurring requirements are:

- o data on reactive systems,
- o data to as high a temperature as possible,
- o data using small sample sizes, and
- o data obtained using short residence times. Accuracy and precision at or above present level must be maintained.

The report addresses the interrelationship between thermodynamics, kinetics, and catalysis selection and development. The thermodynamic study of organometallic compounds will have far reaching implications in the whole field of catalysis.

A chapter outlines the major differences between light petroleum and heavy petroleum, shale oil, tar sands, and coal liquids highlighting problem compounds. The report also reviews other sponsored reports on the needs of the fuels industry; the present report differs from them in its emphasis on economic factors and the coverage of all the alternate fossil fuel sources. The report closes with a chapter outlining the active thermodynamics research groups within the United States.

An accompanying document outlines a five-year plan for thermodynamic research in fossil energy. The plan, based on this assessment, prioritizes the tasks necessary in obtaining the relevant thermodynamic data and deriving the corresponding correlations necessary for the continued highly efficient and economic production of energy from our sources of fossil fuels.

1. ENERGY OUTLOOK: A REVIEW OF EXPERT OPINION

In the present situation of falling demand and price for light crude petroleum, it is difficult to envision the need for other sources of petroleum type fuels. However, such will be the need. This chapter outlines the views of some experts on the world energy situation and serves as an introduction to the remainder of the report. It gives us a possible time scale for future developments in the petroleum industry.

The United States dominated the world petroleum market and was a net exporter of petroleum products until the early 1950's. Then it became a net importer with imports increasing each year. The crude oil disruptions of 1973 and 1976 led to conservation methods. Since these two disruptions, and the tenfold increase in the world market price of crude, remarkable changes have taken place in the consumption and production of the fuel slate. In 1976 the United States consumed about 17.5 million barrels of oil per day and imported about 41 percent of the amount consumed. The current consumption is about 15 million barrels per day with about 30 percent being imported. In a Conoco (1985) report (1), "World Energy Outlook Through 2000," it is stated that imported oil will again jump to 43 percent of the United States oil demand by the year 2000. Chevron in a recent (1985) report (2), "World Energy Outlook: 1985-2000," draws a similar conclusion as regards to consumption. The latter report also states that of the estimated 698 billion barrels of proven oil reserves at the year end 1984, the United States had only 27 billion barrels, and OPEC held 476 billion barrels. A Gas Research Institute (GRI) study, "Description and Implications of the 1984 GRI Baseline Projection of United States Demand for Liquid Fuels," charts the outlook for crude oil demand, projected domestic and imported supply, and petroleum product imports to the year 2010. This report projects imports as high as 9.2 million barrels of oil per day by 2010, higher than during the last oil crisis.

GRI president Henry Linden says long-term planning and public policy should "include scenarios that do not presume extended petroleum availability at moderate prices. If growing United States dependence on oil imports again proves untenable, new government policy initiatives are likely to be implemented that could lead to a significant redistribution of demand among energy sources."

The head of Peat Marwick's oil and gas practice, V. K. Maultsby, Jr., has recently spoken of this reliance on imported fuels (4). He notes that "What is lacking is a sense of total national security -- composed of military security, economic security, and energy security. All three are closely related. Without military security our economy would be endangered. Without a strong economy, our military strength would be endangered. Without a wise energy policy, neither a strong economy nor an effective military program can be sustained."

At present, it is difficult to attempt to define a United States "energy problem" or a global "energy problem" when most of the world perceives that there is an adequate supply of oil and gas. However, the supply is finite, and it is being diminished at a much faster rate than new energy sources are being introduced. The present abundance of petroleum products is a result of reduced demand brought about by a world-wide economic recession, some fuel switching, and some good conservation measures. Also, in some areas oil production has increased; e.g., United Kingdom and Mexico. In the United States by the year 2000, we will have pumped 90 percent of the petroleum products available by standard techniques from the ground (5). In fact, production peaked in 1970 in the 48 lower states. Similarly, most analysts believe world production will peak somewhere between the years 2000 and 2010 (5). If they are even reasonably correct, there will be only decline in the present petroleum industry in the twenty-first century, and the industrialized nations need to make some important energy decisions. The outlook is for declining supplies and skyrocketing prices with disastrous tensions and strains on international relations.

The potential of the world's significant oil provinces has been updated by Ivanhoe (6) in a recent article in the Oil and Gas Journal. He paints a bleak picture, and while the situation may not be as bad as he states, three quotes from his article are relevant here. First, "Our globe's oil age will effectively end during the lifetimes of many persons now alive . . ." and "we must not forget that other nations develop their oil for their own needs--not for the United States." He finished his article with "It is later than you think, and time is no longer on our side." Ivanhoe's figure 4 (figure 1.1) relating world crude production to population explosion is a salutatory experience.

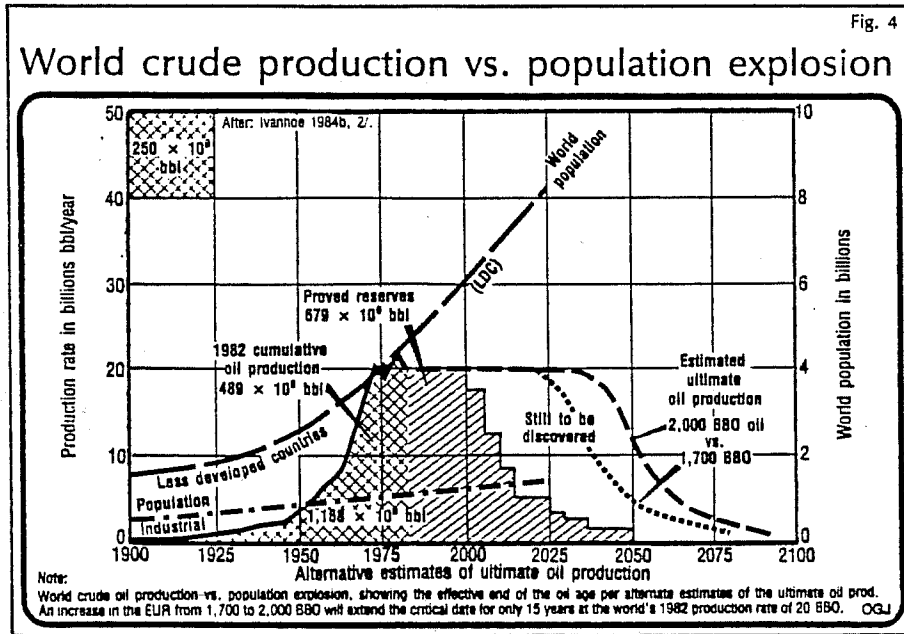


FIGURE 1.1. World crude production versus population explosion reproduced from reference 6.

In the United States at present the fuel slate is also undergoing a change. The pattern of consumption is to a higher ratio of jet and diesel fuels versus gasoline and a lower production of residual fuels. However, at the same time that product demand has been shifting to a more hydrogen rich mixture, the available crude supply has been shifting to a more hydrogen deficient mixture (7). Most of the major crude oil discoveries in the United States in off-shore California and the Gulf of Mexico have been heavy crudes, and the world producers in general are now producing a large proportion of their crudes as heavier crudes. At present the low price differential between heavy and light crudes has discouraged refiners from initiating projects to refine heavier crudes. However, in the long term the predominance of heavier crudes in the world will ensure their conversion. Development of the most efficient pathway for converting residual oils to high quality transportation fuels will be the major growth area in petroleum refining.

Since 1977 the market for residual oil in the United States has dropped from 3 million barrels per day to 1.4 million barrels per day. The heavy boiler fuel market probably will not recover this lost ground, and future refineries will need to produce less residual fuel to be economically viable. In the short term (remainder of the century), the United States petroleum industry needs to be able to refine heavy crudes as economically as the present sweet light crudes if it is to be able to remain a major factor in the world oil market and not lose ground to the Middle East.

In the longer term the United States (and the rest of the world) needs to develop other energy sources previously considered not feasible for commercial use. Extensive research is underway to provide solutions for successfully refining of oils from sources such as shale, coal, and tar sands. A considerable part of this effort is expended to develop suitable techniques to obtain the oil from these new energy sources. A parallel effort is underway to evaluate the suitability of available refining technology and develop new methods for upgrading these new fuel sources. However, the whole synfuels industry is still in its infancy, and the Conoco report (1) states that although synthetic fuels use will increase by more than 10 percent a year over the period to the year 2000, it will account for less than 1 percent of the total energy supply.

The shale oil resources in the Western United States (mainly in Colorado, Utah, and Wyoming) are extensive, and the potential recoverable resources based solely on technical capability, without regard to economics, are large. An estimate of production of 8 million barrels per day for over 200 years has been made for a 15 gallons per ton (GPT) resource (8). In addition, eastern shale oil deposits have been estimated to be capable of yielding another 200 billion barrels of oil from sources with more than 10 GPT.

Identified United States coal reserves (9) are estimated as 1.7 trillion tons of coal occurring at depths to 3,000 feet and thicknesses of at least 14 inches. Present economic factors limit the amount of recoverable coal to 232 billion tons, and at present consumption rates this would mean sufficient coal for 400 years. However, if these reserves are used to make liquid fuels, the production rate will increase with a consequent decrease in its lifetime. Processes for producing liquid fuels from coal have been known for over 50 years. These processes have never been economically competitive with the large supplies of relatively cheap liquid fuels from petroleum, and they are known to be very wasteful of energy potentially available from these sources.

The main United States future energy policy objective must be to protect our economic and national security by developing these new energy resources. However, two other objectives are almost as important. They are:

- (1) To ensure that while exploring the new resources, we protect our environment.
- (2) To minimize the social and economic costs of energy production and bring about acceptable energy prices.

There are major differences between the various crude liquids obtained from oil shale and coal. The most important is hydrogen content. The hydrogen/carbon (H/C) ratio in oil shales like petroleum crudes varies between 1.6 and 1.8, but, in coal liquids, it is normally in the range 1.0 to 1.2. A typical fuel in use today has a H/C ratio of 1.7 to 1.9. Diesel engines and home heating furnaces have difficulty in burning fuels with a low H/C ratio. However, the relatively low hydrogen contents of aromatic fuels may be advantageous for use in spark-ignition engines.

Hydrogen must be added to the various crudes during refining to increase the H/C ratio, but this is expensive and energy intensive. The thrust in future technology must therefore be towards the most efficient use of hydrogen to achieve a given product composition. Also, it may be more economic to use the different crudes to make a few products and not the whole range of fuels. Petroleum crudes are used to make gasoline, jet and diesel fuels, heavy fuel oils, and aliphatic petrochemicals. Shale oil would be most reasonable for the manufacture of jet and diesel fuels, although the others are also well suited. Coal liquids, in contrast, are better suited for manufacture of gasoline and heavy fuel oils, but poorly suited for jet and diesel fuel or aliphatic petrochemicals.

Coal or coal char can also be converted to a CO/H_2 mixture which can, by catalytic conversion, be made into a variety of hydrocarbons, alcohols, and other chemicals. For high hydrogen content fuels, this may be the appropriate route to their manufacture.

Regardless of the alternate fuel situation, it is worth remembering that there will be little incentive to build new, expensive refineries to process these fuels, and conversion of present refinery capacity will be the most economic way forward. Existing petroleum conversion and separation technology will be appropriate for final processing of the new fuels assuming problem compounds are converted beforehand.

The Pimentel report, "Opportunities in Chemistry" (10), puts the present/future energy situation in prospective as follows: "Ninety-two percent of our present energy consumption is based upon chemical technologies: this will remain true well into the 21st century. However, new chemistry-based energy sources have to be tapped. They will include low-grade fuels for which better control of chemical reactivity is needed so we can protect the environment while providing energy at reasonable costs."

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2. FEATURES OF THE FUEL INDUSTRY OF THE NEAR FUTURE

Having at its disposal the necessary engineering skills, knowledge, and experience the American petroleum industry is fully capable of meeting the challenges of the future. Nevertheless, the production of the present fuel slate from heavy petroleum, shale oil, coal, or tar sands is not a straightforward extension of existing technology. In the short term the processing of heavy petroleum must be undertaken while maintaining the present 95 percent energy efficiency of the refining industry in general. Economically, this means that the industry must (1):

- (a) ensure that it produces no by-products of less value than the crude
- (b) produce its requirement of hydrogen efficiently
- (c) minimize its energy requirements

In the longer term the alternate crudes from shale oil, coal, and tar sands will be used to produce synthetic fuels. The production of synthetic fuels from solid raw materials differs from petroleum processing in the variety and types of compounds which are present in the form of very complex mixtures, often containing several hundred identifiable components. This means that processing conditions will be different from those required at present in the petroleum industry. At present the ranges of temperature and pressure encountered are -50° F to 1200° F and ambient to 1000 psi, respectively. Recent proposed synthetic fuel processes have required -50° F to 4000° F and ambient to 3000 psi, respectively. The severity of the operation conditions means that synthetic fuel plants would be extremely expensive. An estimate of an investment of \$5 billion (1981 dollars) for an economically feasible plant for synthetic fuels manufacture has been made (2). Chevron Research Company (3) in a recent report, in the series "Refining and Upgrading of Synfuels from Coal and Oil Shales by Advanced Catalytic Processes," has revised cost estimates to 1984 dollars. In this report the costs of the refining plants alone are of the order of \$1 billion for an output of 50,000 barrels per day. Therefore, everything possible ought to be done to utilize the lead-in time to major synthetic fuel manufacture in the United States to perform all the research that can contribute to the increase in efficiency at the different stages of design and construction of such plants and hence

reduce costs. The goal should be the design of processes which lead to products that can be used in the present refinery system, or, refineries containing suitable cost effective modifications.

It is not the purpose of this assessment to give overviews of the present technology in synthetic fuel manufacture. The reader requiring such information for a particular process is referred to the Handbook of Synfuels Technology (4). For detailed studies on refining and upgrading synfuels from coal liquids and shale oil, the series produced by Chevron Research Company for DOE on Paraho shale oil, West Virginia SRC-II oil, Illinois H-Coal oil, Wyodak H-Coal oil, and Texas Lignite EDS oil are the most comprehensive (5). References 6, 7, and 8 also contain concise assessments of the present technology.

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3. THE ECONOMIC IMPACT OF THERMODYNAMICS

Thermodynamics deals with all forms of energy and matter and with their transformations. Every process and every reaction that occurs can be subjected to the powerful scrutiny of thermodynamics. Therefore, to build an efficient plant which works at maximum efficiency, i.e., uses the lowest amount of energy to produce a given product, thermodynamic data are required. The uses of thermodynamics and its importance in the real world in which we live continue to be a mystery to the lay public and even some chemists and engineers. This is in spite of a number of national conferences in the recent past which dealt specifically with the need for and uses of thermodynamics (1-4). However, this is true of the whole of chemical sciences as outlined in the Pimentel report, "Opportunities in Chemistry" (5).

Any spontaneous process occurring in nature and any artificial process run in industry are both strictly constrained by the laws of thermodynamics. These laws allow us to describe the initial state, the direction of transformation, and the final state of the system. The energy balance of the process and the most convenient and economic route to the desired result are also shown by thermodynamics. Beyond the scope of thermodynamics go only the description and modifications of the process rates which are the realm of chemical kinetics and catalysis.

A prominent and practical application of thermodynamics is the calculation of free energies and hence equilibrium constants for reactions, elucidating their feasibility. The history of many industrial manufacturing processes reveals that the process would not have been possible without knowledge of the thermodynamic properties. Design of new technological processes requires the knowledge of a number of thermodynamic properties over a wide range of temperature and pressure to be able to make a reasonable choice from among alternate solutions.

The best flagship of the need for and uses of thermodynamic data is the petroleum refining industry itself. The light petroleum refining industry is about 95 percent energy efficient, significantly better than most other industrial plants. How is it in such an efficient state? An important contribution to reaching this high level of efficiency has come from the American Petroleum Institute Research Project 44, started in 1942, and other data acquisition and evaluation projects sponsored by API and various individual

companies. This fundamental data enabled the petroleum refiner to be able to fix values of temperature and pressure to achieve optimum results in his refining operations. These processes include the following: fractionating processes, thermal cracking, catalytic cracking, isomerization, alkylation, polymerization, hydrogenation, dehydrogenation, cyclization, and dehydrocyclization. The fundamental data, relating to chemical equilibria among hydrocarbons, have given the petroleum industry an almost magical power to produce needed substances in the proper amounts at will. The cost of the data acquisition and assessment was only a miniscule part of the economical benefit to the country.

Will the refinery of the future continue at this high efficiency? It is clear that the economic well-being of the country may depend on the answer being yes. J. R. Murphy, manager of process technology for Pullman Kellogg, has outlined the changes ahead for tomorrow's refinery (6). He states that:

- o "There will be no by-products having less value than the crude. Production of residual fuels will discontinue.
- o There will be considerable hydrogenation and desulfurization facilities, and the hydrogen required must not come from the desired products.
- o It must contain features which minimize energy requirements.
- o The refinery must also be capable of working with a range of crude fuels."

These are tough constraints to put on the operation but are realistic for continued economic viability. The present petroleum chemical thermodynamic data will not be sufficient to meet these requirements. For example, the API 44 project data on polycyclic aromatic compounds ended with some naphthalene derivatives, and coal liquefaction processes require data on condensed systems with up to at least six aromatic rings present. In addition, the development of new suitable techniques to obtain oil from shale or coal and the refining of the products by new techniques will require thermodynamic data on a range of compounds not encountered before in refining technology.

One can describe two extreme approaches to the development of the new processes needed in the processing and refining of the alternate crudes. The first is the trial and error approach that would test all conceivable procedures, whether or not they conform to the laws of thermodynamics. It has

worked in the past, but it is inefficient, expensive, and succeeds only a fraction of the time. In contrast to that approach one can use thermodynamics to eliminate impractical processes, to characterize the limitations of each possible process, and to specify the design criteria that must be met by the materials used in the process. This approach eliminates expensive testing of materials and the possibility of building plants for processes which cannot possibly work; i.e, violate the second law of thermodynamics. However, to succeed, the second approach requires thermodynamic data which are accurate. This requires both expertise and time. At present the world fuel situation means that we have both on hand, but this may not be the position in the future if the wrong decisions are made now. Headstrong developments, pushed by political pressure for short-term results, that are unlikely to contribute to any real advances in dealing with our energy problems, should not be undertaken. They are not only unlikely to make any long-term contributions; they are detrimental by diversion of money and manpower from the several long term projects. It must be emphasized that any substantive developments are necessarily long-term objectives and that the time to strengthen the background of fundamental knowledge is now and not when the problems are at hand.

To emphasize the last statement, it is worth noting the remarks of G. R. Hill (7). At a recent conference on the future direction of coal research, Professor Hill stated that "The integration of new concepts into commercial plants on a significant scale, based on research results, takes decades, not months or years, to accomplish. There is a minimum of ten years delay between making a decision to build a synthetic fuel plant and the availability of its products for our transportation and heating systems."

In science, as in all other facets of life today, the concept of cost-effectiveness arises. We must articulate our convictions of the needs for thermodynamics in quantified terms of dollars and cents. In other words, what is the economic value of the data? Paradoxically, the full value becomes evident only if we assume:

- (1) the consequences of the absence of data.
- (2) the consequences of the lack of confidence in data that happen to be available.

- (3) the consequences of the fact that "unreliable data can be worse than no data at all."

In the face of unreliable data or lack of confidence in that obtained, the designer adopts a defensive strategy and overdesigns by incorporating larger than necessary safety factors to achieve success. While it is easy to calculate the amount lost when a plant does not work, it is impossible to estimate the economic loss in a plant which works but is overdesigned. It is difficult to give concrete examples of "failures" as these are almost never advertised in print, but most chemical engineers are aware of the problem.

In June 1980, an article in Hydrocarbon Processing (8) discussed the impact of poor or nonexistent data on the cost of coal gasification plants. In the article the Supplemental Gas Committee of the Gas Processors Association stated that in a plant costing \$3-4 billion the overdesign necessary to alleviate the poor or nonexistent data amounted to \$100 million. Ten of these plants give a waste of \$1 billion. The committee pointed to similar problems in coal liquefaction and drew attention to the inapplicability of present petroleum correlations to extrapolate data because of the extremes of temperature and pressure encountered in liquefaction and the abundance of compounds containing oxygen, nitrogen, and sulfur. The committee estimated that the cost of obtaining the required data to eliminate the problems would only be 5 percent of the cost of the overdesign of one plant. These estimates were only associated with those for a process with an accepted scheme of conversions. If one considers the possible economics that may arise from more judicious applications of chemical thermodynamics, the potential economics give promise of much greater saving.

At a recent meeting of Chemical Industry Engineering Society of China and the AIChE in Beijing, China, September 1982, E. J. Miller and F. M. Geist (9) presented a paper "Impact of Recent Developments in Thermodynamics on Chemical Process Design." It contained three case studies one of which, cryogenic hydrogen purification of refinery gas, is relevant to the discussion here. Cryogenic hydrogen purification processes provide high purity hydrogen which is necessary for hydrotreating, hydrodealkylation of aromatics, hydrodenitrogenation and hydrodesulfurization of petroleum feedstocks in refineries. The typical feed stream to the purification process contains hydrogen mixed with

hydrocarbons and other gases which are removed in the cryogenic step. In a plant built in 1961, a liquid nitrogen refrigerator was included in the design because uncertainties in thermodynamic properties required a degree of conservatism to ensure adequate refrigeration to meet guaranteed performance. Using new, more accurate thermodynamic data, it could be shown that the plant would work without the nitrogen refrigerator. They are not included in present designs, and in a plant costing \$22 million that means a saving of \$1 million. The cost of obtaining the data is not given in the paper, but it will be a miniscule portion of the total savings to the refining industry, particularly when they convert to the new alternate crudes and hydrogen importance increases.

At the 1985 spring meeting of the American Institute of Chemical Engineers, a session was devoted to Thermophysical Property Research in which a number of papers highlighted the economic importance of property measurement and correlation. Notable among the presentations was that of M. A. Albright, Phillips Petroleum Company (10). Without naming specific processes, he related knowing of a case where an attempt to violate the Second Law of Thermodynamics resulted in several very large plants requiring several years and millions of dollars before they ran properly. Albright stated that \$1,500,000 rested on the prediction of a bubble point for a cryogenic plant within 1° F, and \$35 million was the penalty for not questioning the data used in another design.

Albright also stated: "If we as a group (meaning industrial users of the data) do not make others aware of errors and pitfalls, we cannot expect their support in funding our research." We agree wholeheartedly with this statement. More details of the economic benefits of thermodynamic data, the consequences of its lack or misuse, and the consequences of it being in error should be published and drawn to the attention of those funding such research. It is realized that much work in the field is proprietary. It is hoped, however, that its proprietary nature could still be upheld in confidential communications with funding agencies like NSF and DOE. The result of industry's constraints in indicating benefits of experimental thermodynamic property measurements in this manner has led in part to what Albright has stated: "Experimentally, thermophysical properties are in deplorable shape. The number of laboratories in America is shrinking. The number of

laboratories capable of wide temperature and pressure and chemical variations is minute compared to the needs. The number which turn out high-precision, high-accuracy data is even smaller. The number of people skilled in the art of measurements is decreasing. Technicians are incapable of replacing these people because they lack the scientific understanding and thermodynamic knowledge required."

In a recent engineering evaluation of the nonintegrated two-stage liquefaction (NITSL) process for coal prepared by Sterns Catalytic Corporation for the Electric Power Research Institute (11), the lack of thermodynamic data was highlighted in the section on critical areas of design and reliability. We reproduce the complete paragraphs here.

Scale-Up Risks

Scale-up of the NITSL process from the pilot plant level to 15,000-tpd capacity involves two major risks: (1) derating of the plant due to a lack of thermodynamic data on coal liquids; and (2) problems with equipment scale-up.

Lack of Thermodynamic Data for Coal Liquids

When equipment is designed for heat transfer or phase separation, the reliability of the design depends upon knowledge or relevant thermophysical (enthalpy, viscosity, and density) and phase-equilibrium properties. In petroleum refining, considerable data and correlations have been developed over many years, which makes predicting these properties almost risk-free. However, the relatively new field of coal refining "is supported only by tenuous data and inadequate design practices, owing to a relative lack of experience with coal fluids." Petroleum-based correlations of thermodynamic properties are unreliable for predicting data for the NITSL process, because they do not account for the aromatic nature of coal-derived liquids or the presence of heteroatoms.

The major risk associated with the lack of thermodynamic data on coal liquids is possibly derating the plant because of undersized equipment. Errors in the thermodynamic data used to design plant equipment will not prevent its operation. However, if, for example,

heat duties or vapor flow rates are underestimated during design, the installed equipment will be unable to accommodate the process streams at design flow rates. To ensure an adequate safety margin in equipment design, a conservative design philosophy was established in all areas of the plant that handle coal slurry or coal liquids.

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4. THE POSSIBLE ECONOMIC IMPACT OF THERMODYNAMICS ON PROCESSING ALTERNATE CRUDES

What are the present economics of production and refining heavy petroleum, shale oils, coal, and tar sands? Where can thermodynamics improve the economics? These are two of the questions to which answers are required by DOE in ascertaining the cost effectiveness of future thermodynamics research in this field. The number of methods of production of a crude oil from its solid precursors and its subsequent upgrading to a finished fuel are many and varied (e.g., see reference 1). In the case of heavy petroleum upgrading, some of the overall possibilities can be outlined as follows:

CRACKING

THERMAL CRACKING

VISBREAKING

COKING

DELAYED, FLUID, FLEXI

HYDROCRACKING

CATALYTIC CRACKING

SOLVENT EXTRACTION

SOLVENT DEASPHALTING

SOLVENT DENITRIFICATION

HYDROTREATING

Therefore, attempting to answer the first question is difficult as, to our knowledge, no overall economic analysis exists, and those presented in the literature comparing several processes for a single crude are not closed systems. They are nearly always open-ended, thus failing to give accurate cost for some input materials, e.g., hydrogen for upgrading, or they set unrealistic prices for products; e.g., high sulfur/nitrogen containing coke. In refining heavy petroleum or synfuels the hydrogen requirement far outstrips that obtained in the catalytic reformer. The market for coke with high sulfur and nitrogen content is small at present and, with stricter SO_2/NO_x environmental restrictions, is likely to vanish.

In recent years a number of economic analyses for upgrading/refining heavy petroleum have been published which use as an example heavy Arabian crudes (2,3). This is not typical of the heavy crudes of the United States and the analyses are, therefore, poor baselines. An exception to the above

general statement is the recent report "Upgrading Heavy Crude Oils and Residues to Transportations Fuels: Technology, Economics and Outlook" prepared by S.F.A. Pacific, Inc. In that report the various processing methods were compared for selected crudes, and plots of net realization versus coke, pitch, or excess fuel gas value were made. At zero value for the by-products, hydroprocessing/hydrocracking methods were the most economic. Regardless of the production or refining methodology, the same problem areas affect the overall economics the most. These problem areas are hydrogen requirements, the need to remove large amounts of heteroatom compounds, the presence of metals, and coke formation reducing yields. The degree of importance of each of the above four problem areas varies with the crude, but all four are always present. Equally important is the methodology used to produce crude oil from the alternate fuel sources. Present proposed processes for the production of oil from shale and the liquefaction of coal are energy intensive and uneconomic. In the following sections each problem area is considered in turn, outlining its importance to the overall economics and where thermodynamics can improve the situation. The first two problem areas, hydrogen requirements and removal of heteroatoms, are closely related and can be discussed together.

Hydrogen Requirements/Heteroatom Removal

Table 4.1 (reference 5) gives the relative hydrogen consumptions for various reactions in refining of crudes. The large amount required for nitrogen removal stands out. Hydrogen can be provided in three basic ways:

- (1) As a by-product of catalytic reforming in producing gasoline.
- (2) Through steam refining and cracking of gases and light petroleum products.
- (3) From the partial oxidation of heavy residual fuel oil, coke, asphaltenes, or coal.

Cornell and Hernzelmann (6) have projected hydrogen needs to the year 2000. They state that "when hydrogen is used for hydroprocessing of gas oil (heavy distillate or atmospheric residuum), large quantities of high purity hydrogen (95%+) are required as inputs to these plants, and the by-product hydrogen from octane improvement reformers is not adequate." If the hydrogen requirement for petroleum processing for year 2000 was manufactured by steam refining, they estimated that the U.S. crude oil consumption necessary would

be 3.2 percent of that imported that year under best conditions. If hydro-processing was the main heavy petroleum conversion method, this would rise to greater than 9 percent of the imported oil. Hence, methods of reducing this hydrogen consumption are critical to production of low cost fuel, as are methods for optimization of hydrogen production methodology. Similar comments in a different context have been made in reference 7.

TABLE 4.1. Chemical hydrogen consumption^a

Reaction	Hydrogen Consumption scf/b
Sulfur removal	95-100 per each 1 wt %
Nitrogen removal	300-350 per each 1 wt %
Olefin saturation	9 per each 1 vol %
Polyaromatic saturation	27 per each 1 vol %
Hydrocracking	25 per each 1 vol %

^a From reference 11.

The high aromatic content of each of the low-grade feedstocks means that hydrogen consumption will of necessity be greater than for refining the light crudes. Engines which can tolerate lower hydrogen contents, e.g., automotive gas turbine, Stirling, and stratified-charge engines, are unlikely to be widely used in the near future. Hydrogenation of the polynuclear aromatic systems is therefore important, but methods of selective hydrogenation could lead to decreased hydrogen consumption and increased distillate yield on subsequent cracking. This is an area where kinetic measurements could lead to the development of new catalysts. However, little is known about the stability of hydrogenated polycyclic aromatics, particularly those containing three or more aromatic rings. Thermodynamic measurements are required first to show if the search for a suitable catalyst is realistic.

The aromatic content of products from hot water extracted tar sands is markedly high, making it particularly difficult to refine by present methods. Refining methods used at present require high temperatures with large amounts of coke formation, and this problem will be discussed again under the section on coke formation.

Turning to heteroatom removal, this is an area where hydrogen consumption is high. The heteroatom content of heavy petroleum, shale oil, coal liquids, and tar sands is much higher than that encountered in light crudes. The heteroatoms need to be removed for a number of important reasons. These include:

- (1) their retention leads to increased catalyst poisoning and deactivation, particularly in catalytic cracking,
- (2) increased coke formation,
- (3) fuel instability and incompatibility,
- (4) corrosiveness,
- (5) higher probability of toxicity and mutagenicity, and
- (6) failure of fuel to meet environmental NO_x , SO_2 requirements.

The heteroatom content of each crude type varies with sulfur-containing compounds being the most abundant in heavy petroleum, nitrogen compounds in shale oils, and oxygenates in coal liquids although all three are present in all types of alternate fossil fuels.

In heavy petroleum, although the sulfur heteroatom is the most prevalent, the most severe problems are presented by nitrogen removal. Denitrogenation occurs only after saturation of the associated ring structures. Consequently, hydrodenitrogenation is a large consumer of hydrogen. The nitrogen compounds deactivate the catalysts and require high temperatures and higher pressure for successful removal. Even then, certain types of nitrogen compounds remain, particularly pyrrolic types. A review of the problem components of heavy petroleum crudes has been prepared by Anderson and Wells (8).

In shale oils removal of nitrogen is critical because of its effect on downstream processing. The process conditions used at present for even partial removal are more severe than those of present refining operations. High pressures (2000 psi) and high hydrogen consumption (2000 scf per barrel) have been stated (9) as being necessary to reach desired nitrogen levels. Although this is technically feasible, the cost would be very high.

In coal liquids the nitrogen compound removal problems remain, but they are compounded by the presence of large amounts of oxygenates. The role of

oxygen compounds in refining steps like hydroprocessing is not very well known due to difficulties in analysis of oxygen compounds. The previously believed ideas that under mild hydrotreating oxygen compounds were removed from crudes have been questioned (10). Hydrodeoxygenation reactions are now thought to occur either directly or by prior ring hydrogenation, depending on the temperature at which the process is being run. Thermodynamic measurements should help elucidate the situation.

In tar sands the heteroatom content is not apparently higher than in conventional crudes. Their removal, however, is considerably more difficult and is expected to require high severities of treatment with high hydrogen consumption.

New processes for removal of heteroatoms from crudes are urgently required. The situation can be summarized by two quotes from a paper by Katzer and Sivasubramanian (11). Talking about nitrogen removal they state that even a 20 percent reduction in hydrogen consumption would result in an enormous saving. Assuming an average consumption of 2500 scf/bbl for the hydroprocessing step for a commercial level of operation of two million barrels of oil per day (13 percent of our present consumption), a 20 percent reduction in hydrogen consumption would result in a savings of around \$3 million per day. Estimating catalyst requirements based on measurements of deactivation on H-coal upgrading for again a two million barrels per day commercial operation, the projected catalyst requirement would be 10 million barrels per day. This large catalyst requirement represents rates of production far in excess of current levels and requires several times the current world production amounts of cobalt and molybdenum.

Some, if not all, of the above problems arising from heteroatom content can be solved by the joint efforts of kinetics and thermodynamics. Thermodynamics can point the way to possible reactions for which the kineticist can then try to find a catalyst. With a data base containing key compound types (particularly those difficult to remove by the present methods) and their partially hydrogenated products, thermodynamics can show the equilibrium species present for a given process and hence prevent the futile search for a catalyst which disobeys the second law of thermodynamics. Also, with a sufficiently wide data base, the thermodynamicist can point to problem reactions to be avoided. One such reaction comes from recent work at NIPER

which shows the thermodynamics of the reaction of nitrogen compounds with oxygen to form n-oxides which are difficult to remove and which react to form species which are more resistive to conversion. At present, not enough is known about the thermodynamics of these heteroatom compounds to even say with certainty what is the optimum temperature and hydrogen pressure for their removal using present methodology. Calculation of thermodynamic data via additivity and other predictive schemes has produced results which are woefully in error because of the lack of an experimental data base. Good experimental data for the heteroatom compounds and their hydrogenation products are greatly needed.

Presence of Metals

High concentrations of metals in crudes, particularly heavy petroleums, lead to catalyst deactivation by deposition of the metal on the catalyst surface. Some crudes, e.g., heavy Venezuelan and heavy Californian, cannot be refined in residual oil refineries like the Phillips Petroleum Company Sweeny and Borger, Texas, refineries because of their high metal content (12). The amount and distribution of organometallic compounds in crude oils depend on the crude, but in general the heavier and higher boiling the crude, the higher the metallic content. The metals are usually distributed between porphyrin- and nonporphyrin-type structures with relatively high amounts of the former when nickel or vanadium are the metals. In hydrotreating these metals are deposited on the catalyst and are sulfided by hydrogen sulfide from hydrodesulfurization. The catalyst pores then become clogged and the active surfaces are obscured, reducing activity.

Many conflicting opinions exist as to what types of nonporphyrin structures exist, although there are indications that they may cause more severe problems than the nitrogen-containing structures. Studies by Agrawal and Wei (13) on the hydrotreating of a white oil doped with a pure etio-porphyrin show the possibility of reversible hydrogenation reactions before demetallization. Certainly pyrrole-type structures are produced, and the problems discussed above for heteroatoms arise once again since pyrroles are particularly difficult to remove by hydrodenitrogenation, and their presence in fuels is particularly detrimental (14).

In shale oil the main organometallic impurities are arsenic compounds which again poison catalysts in downstream refinery processes. In coal liquids, titanium and iron compounds cause problems. Again, the types of compounds present are as yet obscure, and analytical procedures to elucidate the structure types are required.

At present thermodynamics can throw little light on the problems discussed above. The thermochemical properties of organometallic compounds have not been studied in any great depth. The main reason is the complex chemistry encountered. The strengths of various carbon-to-metal (C-M) bonds are in many cases unknown. Some knowledge of carbon-to-metal bond energies would give insights into the various possible reaction mechanisms for the removal of organometallic compounds from crudes. Judicious measurements on key porphyrinic structures would help answer the question of reversible hydrogenation.

Without thermochemical measurements to help the approach to the removal of organometallic compounds, their removal will continue to be a matter of trial and error testing of various procedures until a suitable method is found. As stated before, this method is uneconomic and inefficient. With thermochemical research on organometallic compounds, particularly of the transition metals, and the measurements of (C-M) bond strengths, the insights necessary for the design of catalysts for particular reactions will develop. At present, the whole field of catalyst manufacture is somewhat of an art where compounds are made and their applicability as a catalyst for a particular reaction tested in the hope that one will work. Thermochemistry can, along with kinetics, provide a more rational basis for catalyst selection and development.

Coke Formation

Some methods of processing crudes, particularly heavy petroleum, produce coke: delayed coking, fluid coking, or flexicoking. These methods, when applied to low grade feedstocks, produce a coke which has a high sulfur, nitrogen, and metals content and, hence, is of little value. For the economics of the processing to remain good, the heteroatoms and metals must be removed or their content at least greatly reduced. This was covered above and will not be addressed again in this section. Coke formation also occurs in

those processes where it is not the desired product. This is particularly true in processing of heavy crudes like tar sands where the polycyclic compounds are thought to cause the trouble. Coke formation on catalysts is a major problem in refinery operations and is the chief cause of unsatisfactory performance in catalytic reformers. It leads to lower liquid yields and upsets the critical heat balance (15). In fluid catalytic cracking units (FCCU) some coke formation is needed to keep the process in balance (5-7 percent typically). Changes in feedstock, can mean that this balance is disrupted and problems arise. It has been stated that "In many cases, it is this (the fluid catalytic cracking unit) conversion capability that determines the profitability of a refinery" (3). In today's economic climate the refiner must be able to respond to changes in feedstock and the FCCU must be able to handle a wide range of different crudes. This can only be done if the heat balance in the system is maintained and it runs at optimum conditions for maximum profitability.

It is known that some of the factors that lead to excessive coke formation are high molecular weight, presence of heteroatoms, presence of metal organics, and the interactions between various molecules; e.g. hydrogen bonding. High temperature of processing is also a major factor. As stated above, in fluid catalytic cracking, heat balance is a crucial factor. Table 4.2 (15) lists the enthalpies of some reactions important in calculating this heat balance. This is another example of thermodynamics at work in refining. With the new low grade feedstocks of the future, the present calculations will need to be extrapolated to include a bigger range of reactions and, possibly, different enthalpies of some of the present reactions. The need for further thermodynamic measurements, particularly thermochemical ones, is obvious.

TABLE 4.2. Enthalpies of some reactions important to FCCU operation^a

	$\Delta_r H^\circ$ KJ/mol
Carbonium ion cracking	+33.8
Dealkylation	+42.0
Dehydrogenation	+59.0
Hydrogen transfer	-105.0
Cyclization	-40.0

^a From reference 20.

New processing methods for these new feedstocks could reduce coke formation particularly if they can be run at lower temperatures. Practical experience tells us, and thermodynamics shows us why all organic molecules will be carbonized if the temperature is sufficiently high. Molecules interacting via hydrogen bonding, etc., can lower the temperature of coking as can the presence of polycyclic structures. However, with judicious choice of representative compounds, thermodynamics can map out the paths between the input substances and carbon formation. Processes which will break up the molecular interactions and crack open thermodynamically weak linkages in large molecules without high coke formation and with corresponding increased liquid yields are the goal. To obtain that goal knowledge of the types and strengths of the interactions are required. The latter can only be obtained via thermodynamic measurements. The use of sophisticated chemistry (similar to that using H_2S in coal liquefaction: next section) may drastically reduce coke formation.

Crude Production

In any overall analysis of the economics of future fuels, the cost of production of the feedstocks is also of high importance. In the literature there are few economic analyses which give relative production and refinery costs for the future fuels. Sikonia et al. (16) is an exception, and table 4.3 reproduces their overall economic summary. The large cost of direct liquefaction of coal and surface retorting of shale oil is striking. It is obvious that new processes for the extraction/production of refinery feedstocks from these fuels are required. This point is also implicit in recent publications like the Conoco report "World Energy Outlook Through 2000" (17). It states that "synthetic liquids from coal and shale oil are not commercially viable given the crude price outlook, so they will contribute less than 100,000 barrels per day to domestic supplies by 2000."

TABLE 4.3. Overall economic summary^c
Basis: 100,000 BPCD (15,899 m³/CD feedstock)

Feedstock	65/35% light/heavy Arabian	Boscan	Coal Distillate	Shale Oil
Estimated production costs, \$/B	4.0	8.0	35-45 ^(a)	25-29 ^(b)
Refining costs \$/B	<u>9.1</u>	<u>16.7</u>	<u>7.6</u>	<u>10.6</u>
Production & refining costs, \$/B	13.1	24.7	42.6-52.6	35.6-39.6

^a Includes cost of mining, and direct liquefaction via hydrogenation.

^b Extraction of shale oil via surface retorting.

^c Reference 23.

The long-term research needs for coal liquefaction technologies were last assessed by the Fossil Energy Research Working Group in 1980 (18). Although much research has been done since that report, the coal liquefaction methodology remains uneconomic. Improvements are still required in process simplification. New catalysts for producing high liquid yield at lower hydrogen consumption, and development of processes which operate at lower temperature and pressures are the primary goals. Equally important economically as those above is improvement in quality as well as quantity of coal liquids produced. Thermodynamics has an important input into these areas. Further studies on the thermochemistry of coals and model compounds will give insights into the mechanisms of bond scissions in coal liquefaction. Vapor-liquid-equilibrium (VLE) studies will better define separations of liquid streams and solids from the reaction products during liquefaction. Studies leading to the relative stability of coal liquid components will point to problem compounds where removal will lead to greater overall stability of the product. Gum formation in coal liquids and coal derived fuels is a major problem with possible dire economic results.

New models for coal structure appear at regular intervals in the literature. Of interest is one described by Professor J. W. Larsen at the 1985 ACS Division of Fuel Chemistry Meeting in Chicago (19). A structure for Illinois No. 6 coal proposed by Larsen is macromolecular. The composition of the model C₁₀₀H₈₄O₁₁S_{1.8}N_{1.4} has five hydroxyl groups per 100 atoms of carbon. The

extractable material that is not bonded to the network has an average molecular weight of 900. The number average molecular weight between crosslinks is 3000. Larsen thinks the startling feature of the model is the large number of active hydrogen bond crosslinks in the structural network. In this particular coal, the hydrogen bonds exceed the covalent links by a factor of four! Other coals may have different values. There are good reasons to believe that hydrogen bonding is extensive in heavy petroleum, oil shale, and tar sands as well.

Narayan (20) uses the term "guest molecules" to describe the molecules trapped in the crosslinked macromolecular structure. Using a potassium crown ether (K-CE) reagent, Narayan has selectively cleaved ether and diaryl linkages at room temperature. The analysis of the tetrahydrofuran extract of an Illinois No. 6 coal after reaction with K-CE reagent at room temperature showed the presence of phenols, tetralins, and dihydronaphthalenes with attached polymethylene side chains. These low molecular weight hydrogen-rich structural units are an integral part of the coal. Low temperature reactions will prevent the condensation of such molecules during liquefaction and thus reduce requirements for hydrocracking and coke formation.

New donor solvents to enhance the liquefaction of coal are being proposed; e.g, recent work by Taylor (21) and by Hirchon and Laine (22) using nitrogenous donors and hydrogen sulfide, respectively. Stenberg's group at North Dakota (23,24) is also working in this field using H_2S , CO, and H_2O to improve liquefaction yields. However, little is known about the mechanisms leading to the process improvements using these promoters other than significant increases in yield are obtained. These increased yields are obtained at lower temperatures than conventional liquefaction and are accompanied by a decrease in the production of hydrocarbon gases. Light alkane gas formation is a major cause of unproductive hydrogen consumption in conventional coal liquefaction (18). The amounts of H_2S needed to provide substantial improvements in the liquefaction are relatively small; it appears to function as a catalyst, but results are still too tentative for the possibility to be verified. Hydrogen sulfide is a cheap disposable catalyst generated in coal liquefaction, and its recycle consumes no net hydrogen, but it leads to reduction of hydrogen consumption and lower reaction temperature. H_2S decreases

the tendency for coke formation (23). Further studies on model compounds accompanied by thermodynamic measurements including bond dissociation energies would help to elucidate possible mechanisms for the reactions.

The need for new processes for shale oil recovery was stated previously by the panel on R&D needs in refining coal and shale oils (7). Economic viability for shale oil would be increased either by new recovery methods not involving retorting or by increasing the oil recovery above the 2/3 usually obtained. A recent promising method of the latter type is that devised by TRW, Inc. (24), which claims 90 percent recovery of available hydrocarbons. Research into the bonding forces which hold the oil in the shale and in particular the strength of such bonds may point the way to new processes for its recovery.

The economic impact of thermodynamics on the processing of alternate crudes can be summarized as follows: thermodynamic measurements leading to Gibbs free energies can be used to design new processes which will lead to more efficient hydrogen management, remove or prevent formation of heavy compounds, and prevent excessive coke formation. Both thermodynamic and thermophysical property measurements will lead to efficient confinement, phase separation, and energy use plant designs, thus preventing overdesign leading to gross energy inefficiency or derating of the plants due to undersize equipment.

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5. THERMODYNAMIC PROPERTIES

Table 5.1 lists the thermodynamic properties which are useful in industrial applications. For a particular industrial application, not all these thermodynamic properties are required, and their relative importance changes depending on the nature of the process being considered. In the initial states of the design of a reactor, the thermochemical properties (ΔH , ΔS and C_p) are essential. Further along the stages from process conception until operation the other important properties will be vapor pressure, pressure-volume-temperature, density, and transport properties data. The other data listed may be important only in special cases. In comparison in the design and operation of fractionators, the emphasis shifts to vapor pressure, P-V-T, density, critical constants, and phase distribution data as being important.

The reader interested in the relative importance of the properties listed in table 5-1 is referred to the paper recently produced jointly by the CODATA Task Group on Critically Evaluated Phase Equilibria in Mixtures and the CODATA Task Group on Data for the Chemical Industry and published in the Hungarian Journal of Industrial Chemistry (1). This paper rates the property groups on an arbitrary scale of two degrees: (1) data are essential for a given process and must be employed in accurate process design and optimization; (2) data are fundamental, and knowledge of them is critical for designing a process and for running a given operation. This paper is an excellent account of the relationships between thermodynamics and chemical engineering design and operations. It is a pity it was not submitted to a journal with a more world-wide readership.

TABLE 5.1. Thermodynamic properties required for industrial applications

Thermodynamic Functions

Gibbs Energy G, Enthalpy H, Entropy S
Ideal Gas Thermodynamic Functions

Heat Capacity

C_p , C_v

Phase Transition

Enthalpy ΔH , Entropy ΔS , Volume ΔV

Enthalpy of Formation

Enthalpy of combustion, reaction, solution, or dilution

Orthobaric Vapor Pressure

Vapor Pressure to Critical Point

P-V-T Relations

Density, Virial Coefficients, Acentric Factor

Critical Parameters

T_c , P_c , V_c

Transport Properties

Viscosity, Thermal Conductivity, Diffusion

P-T-X-Y Relations (phase equilibria of mixtures)

Solid-Liquid, Liquid-Liquid, Vapor-Liquid

Before we move from listing the thermodynamic properties required by industry in general, let us say again that overall the most important properties in innovative process design are those leading to the change in Gibbs free energy for the process. If the Gibbs free energy for a reaction in the process scheme is highly unfavorable, i.e., is highly positive, the chemical engineer begins thinking of a new process and proceeds no further with the present one. Only designs with favorable Gibbs free energies are plausible. No one can beat the second law of thermodynamics no matter how good his/her catalyst. For the chemical engineer who may not be designing a new innovative new process, the components which make up the Gibbs free energy are still of importance. Calculations of heat flow in any system require enthalpy and heat capacity data. If a reaction occurs then standard enthalpies of formation are also important. Finally, even though it is not generally recognized, if a process is carried out in which the change in Gibbs energy is excessively negative, then this is a clear indication that most of the available energy for doing work has been wasted.

It will never be possible to measure all the needed properties on all of the mixtures that may be encountered in synthetic fuels and heavy petroleum. This has been true in light petroleum refining also, but industry experts have found that the properties of undefined mixtures there can be accurately simulated. This is done by representing the system as a mixture of carefully selected pure compounds whose thermodynamic and physical properties are accurately known. Extension of this method to the new alternate crudes will be possible. Work on the pure compounds (if selected properly) can lead to methods of close estimation of the properties of other measured pure compounds. A base for future estimation of properties can then be built and used with known uncertainty limits attached.

A strategy for the thermodynamic property measurements can be outlined as follows. A planned program to meet the general needs must have as its goal the ultimate verification of a model or models for the systems of interest that allows the production of the desired properties to a level of accuracy commensurate with the actual need. The first task is to identify the classes of substances and the properties required. The second task is to identify the key molecules and/or mixtures of molecules on which the specified properties must be measured with the necessary accuracy and precision and to identify the

deficiencies in existing models and correlations. Having fixed the properties, substances, and the necessary accuracy and precision required, the next step is to proceed with the measurements and to generate the required models. This work will involve already existing capabilities and also the development of new techniques and equipment for the experimental measurements and theories for models. As the experimental data are acquired, covering the specific properties on the key compounds and mixtures of compounds, new correlations will arise to calculate values of the specified properties for several prototype systems not previously measured. Then appropriate measurements on the prototype systems should be made in order to determine the validity of the correlation method to produce data to the desired accuracy.

At the recent Thermodynamics Research Planning Meeting at NIPER (2) the industrial participants were unanimous in agreeing that the study of the thermodynamic properties of real process fluids was of limited utility, good only for that sample of today. Such studies should only be undertaken as checks.

Figure 5-1 shows the interrelationships between experiment, compilation/evaluation, correlation, prediction, and the chemical engineer. Those producing the experimental data should work in close contact with the data evaluators and theoreticians. This has not always happened in the past and has led to a large number of correlations with little or no validity. With 4,779 equation-of-state variations since 1967 (3), we really do not need any more, or we need a more fundamental approach to this development. What is needed is the development of new methods of characterizing samples and of predictive correlations. These new models will have to work for large flexible molecules and molecules with strongly interacting groups such as phenols and amines. At a recent meeting on Thermodynamics Research Needs for Fossil Fuels at NIPER (2) the statement was made that companies "do not have a good handle" on the characterization of complex mixtures. Better communications between experimentalists, evaluators, correlators, and the industry are required to answer these problems. Industry could help in this field if they could release sensitivity analyses to show where important error limits are in the overall design of a process.

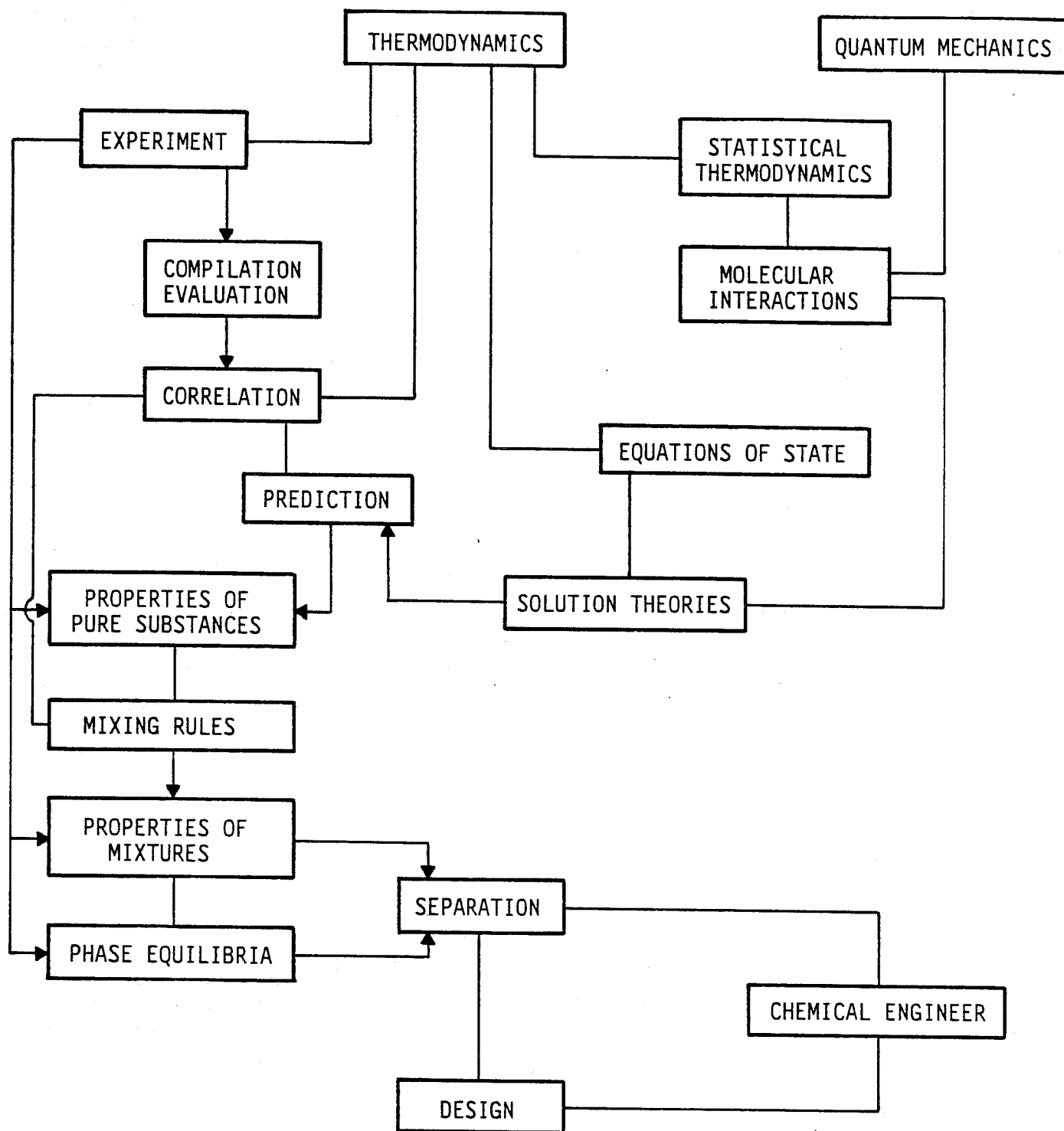


FIGURE 5.1. Interrelationships using phase separation as an example.

As stated in chapter 2, the synthetic fuel processes have been proposed for temperature and pressure ranges from -50° F to 4000° F and ambient to 3000 psi, respectively. Thermodynamic property measurement should, therefore, be over as wide a temperature and pressure range as experimentally possible. This in turn means that the equipment in use at present will need modification or redesigning. New innovative methods of property measurement are also required as much existing equipment requires long residence times at high temperature where pure compounds decompose. Heat capacity measurements to 300 K and vapor pressure measurements to 400 K were common in the past, but present industrial requirements mean such data require long extrapolation with unknown uncertainty.

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6. USE OF GIBBS FREE ENERGY DATA

In the ideal planning of a new process, it should be customary to survey the literature and then, before attempting experimental work, to make a thermodynamic analysis of the system to determine the feasibility of the reaction, and, if possible, ascertain the maximum yield and the optimum conditions for achieving it. This ideal way of proceeding is difficult to follow due to lack of necessary data. Even in cases where the procedure outlined above can be used, it must be remembered that thermodynamics is concerned only with equilibrium conditions. Even reactions with sizable negative Gibbs free energies may proceed slowly in the absence of a suitable catalyst. On the other hand, if the reaction has a sizable positive Gibbs free energy, the search for a catalyst is futile.

Following World War II, the petroleum industry was called upon to greatly increase the output of lower aromatic hydrocarbons for several strategic reasons. The availability of large quantities of hydrocarbons from the petroleum industry made it a logical source of new materials for the products of these aromatics. Two processes, platforming (1) and hydroforming (2), were devised. Table 6.1 compares the C₈ aromatic fractions obtained by both processes with the thermodynamic equilibrium values (3) at the processing temperatures. Note the close agreement with the quantities predicted by the thermodynamic equilibria calculations. In their book, Stull et al. (4), give several more examples of the good correlation of thermodynamic equilibria with experimental and industrial work in the fields of catalytic cracking, hydrogenation, and hydroreforming.

More recently, Linton and Turnbull (5) have made thermodynamic calculations to determine the theoretical equilibrium products for systems relevant to the hydrogenation of coal, and hydrogenation systems in general. Their calculations show methane and aromatic compounds, particularly multi-ring compounds, are very stable. Optimum yields of benzene, toluene, and xylene are obtained at overall H/C in the range of 2 to 3. Multi-ring aromatics can be hydrogenated at an overall H/C > 4 with $T < 800^{\circ} \text{C}$ and $P > 5 \text{ MPa}$.

TABLE 6.1 Composition of C₈ aromatic fractions at 727 K.

Compound	Weight percent		Thermodynamic equilibrium ^(c)
	Platforming ^(a)	Hydroforming, ^(b)	
<u>o</u> -Xylene	23	20	23
<u>m</u> -Xylene	40	43	47
<u>p</u> -Xylene	21	17	21
Ethylbenzene	16	20	9

- (a) Reference 1.
(b) Reference 2.
(c) Reference 3.

Calculations using thermodynamic data on a range of possible compounds like that undertaken by Linton and Turnbull require sophisticated computer programs. Such programs are now being devised and made available to the chemical industry. A further example of new ideas in the calculation of chemical equilibria products is the recent papers by Alberty, et al. (6). Alberty uses the Benson group contribution scheme (7) to calculate data on isomers where values have not been measured.

Cowley and Wiser (8) using the Benson scheme have calculated Gibbs free energies for some of the possible hydrogenation products of anthracene to check the feasibility of converting multi-ring aromatics of three or more rings into monoaromatics via selective hydrocracking of the center ring. Their calculations conclude that such a process is feasible at processing temperatures if a suitable catalyst can be devised. Their calculations will need to be repeated using measured thermodynamic data being obtained at NIPER, since lack of data available to Benson led to a number of approximations in group assignments (see chapter 7).

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7. PRESENT STATUS OF THERMODYNAMIC DATA

Thermophysical Properties

In this section we will not attempt to review the various data available in the literature partly because it is so large and partly because other groups are reviewing the field at present, both here in the United States and in Europe. Attention is drawn to the chapters of the DIPPR Data Production Manual (1) which are excellent sources of available data and correlation methodology. An earlier article in the series on DIPPR activities details gaps in the pure component experimental physical property data base (2). Attention is also drawn to the data collection and evaluation efforts of the National Bureau of Standards Consortium on Supercritical Fluids which has been recently described in the literature (3). In Europe the DECHEMA Chemistry Data Series (4) is the result of industrial and academic collaboration. Volumes on VLE, PVT, critical data on pure components, and evaluated vapor pressures of pure organic compounds have appeared to date (4). The article on "Thermodynamic Data in Industrial Applications" coproduced by the CODATA Task Groups on Critically Evaluated Phase Equilibria in Mixtures and the CODATA Task Group on Data for the Chemical Industry (5) lists 15 references to data projects that have been accomplished or are underway in vapor-liquid and liquid-liquid equilibria alone. This remarkable effort has, at the same time, revealed just how much has yet to be done to have critically evaluated VLE data readily available for chemical engineers who wish to design multi-component real-system distillation columns.

Figure 1 of chapter 5 gave the relationships between experimentation, calculation, and theoretical prediction in the design of phase separators. Similar diagrams can be drawn for other design problems. The need for models for calculation of properties can be exemplified by just considering one case. Suppose we look at 20 compounds; then there are over 21,000 variations in binary, ternary, quarternary, and quinternary mixtures without taking into account the effects of varying composition. Go to 50 compounds and the total reaches well over 2 million without considering varying composition.

In heavy oil processing compounds which had little effect in the past become important. Since the effects are new to the industry, there is little background of data to predict them. Synthetic crude oil processing occurs at

high temperature and pressure. The industrial data base does not cover such areas. Therefore, we cannot answer questions like what should the reactor volume be? - no P-V-T data available, or where will three phases form? - no such data. Secondly, most synthetic crude oil plants involve multiple phases--up to four--no accurate models exist for such systems because of lack of reliable data.

The data requirements for the development of an adequate thermodynamic base for future synthetic fuels and heavy petroleum processing have been reviewed many times in the recent past. References 6 to 8 detail the requirements, and they are not reproduced here again other than to say that they can be summarized as follows:

- o Studies are required on mixtures of light and heavy components including light gases H_2 , H_2S , NH_3 , and H_2O .
- o Temperature and pressure limits should be as high as possible approaching if not passing those used in processing.
- o Compounds studied should take into account the high aromatic content, high olefin content, and high heteroatom content of the synthetic fuels.
- o New, short residence time, experimental methods are required to make the measurements before significant decomposition occurs.

Although the need for experimental data is paramount, we also need to improve our theoretical models. Better physical and chemical models need to be developed to handle strong dipole and hydrogen bonding, molecular geometry, and floppy chain rotations. Many chemical engineers believe that a great many problems would be solved if they had:

1. a truly general equation of state that handled more than one liquid phase and the critical region,
2. a good group-contribution method for every property,
3. accurate critical properties for all substances, and
4. simple correlations for all properties.

This Utopia cannot come. For instance, the measurements of critical properties for large molecules experimentally is difficult and may be in many cases impossible due to decomposition even at very short residence times. New

theoretical methods using pseudo criticals may be an answer here. The current state of the art in correlation of thermophysical properties suffers from two major deficiencies. First, the use of the 50-year-old Watson factor K, specific gravity, and boiling point as inspection parameters for correlation will not work with high-boiling fossil-fuel distillates which contain strong molecular interactions (especially if you cannot determine a boiling point of the residuum). Second, experimental studies are normally on wide-boiling fuels which are not well characterized. New characterization methods are required. These should be based on modern analytical methods, and some work in this field has started (9). Scales of new inspection parameters must be developed from studies on model systems to give quick, easy measures of strong interactions in fluids.

The world of the physical property specialist is centered on the computer. Group contribution methods of data correlation and estimation are ideally suited to computers. The CHETAH program (16) uses the group contribution methodology in estimating thermochemical gas phase properties. The UNIFAC group contribution model is currently used for predicting VLE (10). However, work on the representation of petroleum fractions by group contribution by Ruzicka et al. (11) highlights the lack of current published data to be able to extend UNIFAC to high-boiling fuels.

The strategy for the thermophysical property measurements was outlined in chapter 5. It is worth saying again that the studies are made on a carefully selected set of pure compounds, binary mixtures, ternary, and finally more complex systems chosen to develop models based on well-founded theoretical principles incorporating strong molecular interactions (possibly treated as chemical reactions), effects of molecular size differences, and molecular shape and flexibility are necessary. Correlations and mixing rules need to be developed and to be tested on the specified properties for known prototype systems not previously measured as test cases of methodology and accuracy. Measurements on real process fluids should be undertaken as checks.

Properties Leading to Gibbs Free Energy

Within the list of thermodynamic properties (chapter 5, table 1) is a subdivision known as the thermochemical properties. This subdivision includes measurements made on pure compounds of: enthalpies of formation via enthalpies of combustion or reaction, heat capacities leading to enthalpy changes and entropies, vapor pressure, and enthalpies of vaporization/sublimation either via use of the vapor pressure measurements and the Clapeyron equation or by direct measurement. The combination of all of the above measurements leads to determination of the Gibbs free energy of formation of the pure compounds. Complementary to the experimentally determined thermochemical properties is the calculation of the properties via statistical thermodynamics. Use of statistical thermodynamics provides the thermodynamic functions of a molecule in the gas phase from a knowledge of the molecular partition function (see below), and allows calculation of the properties to high temperature outside the range of the experimental measurements. Statistical thermodynamic calculations are the only answer to obtaining accurate data at high temperature where the compounds under consideration are too reactive to obtain experimental measurements.

The slate of thermochemical properties has not been reviewed recently, unlike the other thermophysical properties. Since we have expertise and our laboratories continue to make significant measurements of the thermochemical properties of organic compounds, we will spend some time reviewing the field in depth.

General Comments

Appendix 7.1 lists the available tabulations of critically evaluated thermodynamic data leading to the Gibbs free energy of inorganic and organic substances. In addition to these tabulations, attention is drawn to the Journal of Chemical Thermodynamics published under the auspices of the IUPAC Thermodynamics Commission that has become a major journal for the publication of accurate experimental thermodynamic data.

Over the years much time and effort have been devoted to obtaining relationships between enthalpies of formation, entropies, Gibbs free energies, and molecular structure. Clearly, if precise, reliable relationships could be established for all types of molecular structures, further thermochemical

measurements would scarcely be necessary, since the thermochemical properties of compounds not studied experimentally could be estimated from their structures. However, even today, while the necessary thermochemical data on some classes of organic compounds are plentiful and of excellent quality, data on other classes are sparse, of poor quality, or totally lacking. In the present state quantum mechanical calculations are not good enough to calculate the required answers, and reliable methods of correlating and predicting thermochemical data can only be obtained via well-established key compound methods. Measurements must be made on a series of key structural types in order to obtain a base from which to develop a method of predicting unknown molecules containing these structural types.

The total energy content of a molecule in its ground state includes: (1) intramolecular energy due to chemical binding of the constituent atoms, (2) translational, rotational, and vibrational energy, and (3) intermolecular energy due to external force fields. Energy from type (3) can be partitioned from types (1) and (2) by specifying properties for the molecule in the ideal-gas state. The evaluation of intermolecular forces is not easy (see section on enthalpies of vaporization/sublimation below); therefore, the common thermochemical property estimation schemes calculate values for the ideal-gas state.

Additivity schemes are not new, the first being introduced by Fajans in 1920 (12). Early schemes were of the single transferable bond energy type and did not reproduce the known data well. The additivity function of structural-group contributions was first shown by Parks and Huffman in 1932 (13) but was not clearly described until 1958 by Benson and Buss (14). The Benson-type additivity scheme as described in "Thermochemical Kinetics" (15) is the best known scheme in use today, and most other schemes can be reduced to it. The ASTM Committee E-27 CHETAH program (16) is a computerized version of the Benson group additivity scheme and is used extensively in chemical industry. If the required groups and correction parameters are available, the program gives good values of $\Delta_f H^\circ$, S and C_p (298-1500 K). However, not all the necessary data are available for calculation of values for a number of types of compounds that are present in heavy petroleum, shale oil, coal, or tar sands. The next section will survey the present status of enthalpies of

formation, entropies, and heat capacities with emphasis on gaps in the Benson calculation methods where lack of data leads, at best, to guesses of group contributions.

Enthalpies of Formation, Heat Capacities, and Entropies

Use of the group additivity scheme to calculate thermochemical properties ($\Delta_f H^\circ$, S° , and C_p) in the ideal-gas state for organic molecules is not simple. Even when all the groups are available, a series of corrections must be applied to allow for the other interactions in the molecule. Overall,

$$\Delta_f H^\circ \text{ or } S^\circ \text{ or } C_p^\circ = \Sigma \text{ groups} + \Sigma \text{ stabilization terms} \\ + \Sigma \text{ destabilization terms.} \quad (7.1)$$

Examples of destabilization terms are gauche 1,4 interactions, 1,5 steric repulsions, ring strain, and electrostatic repulsion interactions. Stabilization terms are a general phenomenon of π -electron systems found in aromatic compounds. Careful consideration of these extra terms is required in calculation of $\Delta_f G^\circ$, S° , or C_p values for compounds whose values are unknown. For example, the correction due to steric effects for 2,5-dimethyl-2,5-diethylheptane is 56.1 kJ mol^{-1} , or 19 percent of its standard enthalpy of formation in the gas phase.

Hydrocarbons

The large quantity of thermochemical data in the chemical literature on alkane and acyclic systems is capable of reproduction by group additivity scheme calculations if cognation is taken of interaction parameters. This may not be true of large bridged-ring systems, but these do not appear to be significant components of heavy petroleum, oil shales, coal, or tar sands. However, crudes from the USSR appear to contain significant quantities of these large acyclic ring systems; e.g., adamantane derivatives (17).

In each of the above fossil fuels, polycyclic aromatic rings form the backbone of the materials, and hence measurement/calculation of their thermochemical properties is of critical importance in process evaluation. The group parameters used for polycyclic aromatic hydrocarbons were published nearly 10 years ago, and because of lack of data, a number of groups were

assigned values. Since that time, through the efforts at NIPER and other laboratories, this data base has been expanded, and a reassessment of the parameters is required. In the partially hydrogenated ring systems the ring correction terms need reassessment as shown by recent measurements in this laboratory where measured enthalpies of formation and entropies for compounds like 1,2,3,4-tetrahydrophenanthrene are compared with calculated values by Benson in 1977 (18). Absence of ring correction terms and a sufficient basic data base led to a number of assumptions which have since proved to be in error. Work at NIPER has shown the estimated values for some molecules were within ± 3 percent of the experimental values in the 350 to 450 K range, which is much too broad an uncertainty to justify using the estimates in chemical equilibria calculations.

A critical evaluation of the existing enthalpy of formation, entropy, and heat capacity data should be made on a compound-by-compound basis. The assessed data should then be used to derive a new set of group contribution terms for use in the polycyclic aromatic systems including ring strain corrections for the partially hydrogenated systems. An important part of the reevaluation of the group additivity parameters is to determine the minimum number of parameters needed to produce estimations accurate enough for equilibria calculations.

Similarly, reassessment of the data on alkyl substituted polycyclic aromatic systems is required including the recent data acquired on naphthyl systems at NIPER (19). The data acquired on polycyclic systems with 5-membered rings present, i.e., substituted indans (20), should also be included in an overall reassessment of the data base.

For the majority of compounds that are essential to the derivation of group values, condensed ring heat capacity studies terminated at or very near room temperature. As part of the critical evaluation of existing entropy data, key compounds should be selected for extension of high precision liquid phase heat capacity measurements and/or vapor pressure measurements to as high a temperature as practicable (250-300° C). Ideal gas heat capacities are needed to be able to calculate the thermodynamic functions at the temperatures of processing, and the group additivity scheme is not nearly as potent without them.

After the reassessment of group values, key compound studies should be undertaken to check the assigned values. Measurements on pure samples of chrysene, 3,4-benzophenanthrene, 1,2-benzoanthracene, and carannule may be necessary to confirm the polycyclic aromatic group assignments. Similar conformational studies on compounds will be required for the other major areas described above; e.g., partially hydrogenated systems. Further studies on close approaching neighboring groups in alkyl phenanthrenes, pyrenes, etc., are necessary.

Oxygen Compounds

Oxygen-containing compounds can account for an appreciable amount of some heavy petroleums, shale oils, tar sands, and particularly coal liquids (see chapter 8). Oxygen can be present as part of many functional groups including -OH, -COOH, -C=O, and -C-O-C- as well as 5- and 6-membered ring structures. Combination of oxygenate functional groups within the same structure are not uncommon (see chapter 8).

The primary sources for condensed phase enthalpies of formation, heat capacity, and vapor pressure measurements for aliphatic alcohols, ketones, and ethers are the publications of the National Physical Laboratory, England, during the 1960's and 1970's. A large number of compounds of each class were studied, so an excellent start on a data base is available. Unfortunately, the condensed phase heat capacity data only rarely extends above 320 K which makes much needed high temperature (500 K and above) correlations impossible. New liquid phase heat capacity and vapor pressure measurements to higher temperatures on a select group from all of these families would be very beneficial, particularly when the speed and ease of good liquid phase heat capacity data are considered.

The National Physical Laboratory is again the primary source for condensed phase enthalpies of formation, heat capacity, and vapor pressure data for phenols. The heat capacity data for the methylphenols was taken to 400 K while that for phenol stopped at 336 K. As with the aliphatic oxygen compounds, liquid phase measurements to high temperature would be most helpful. Data on the 1- and 2-naphthols are questionable for enthalpies of combustion, and no data on their heat capacities exist. Therefore, extension of a group additivity scheme to polycyclic aromatic alcohols is questionable

as it is based on assuming several different groups are equivalent. In other words, the additivity scheme used with the present state of knowledge predicts equal values of $\Delta_f H^\circ$, S° , and C_p for both naphthols which is not true. No data exist on partially hydrogenated polycyclic aromatic alcohols. Such data are required to help elucidate the conditions under which the -OH group can be removed without hydrogenation of the ring system.

Studies on aromatic ethers and ketones are sparse. For example, diphenylether is the only aromatic ether where complete thermodynamic functions exist over an appreciable temperature range. Studies of further key compounds of both types are required to derive groups basic to large ring systems.

Here, ring structures of interest are those containing the oxygen atom within 5- and/or 6-membered rings. The single ring systems have been studied, but data on higher ring systems are rare. In his book, Benson (15) assigns ring corrections for calculation of enthalpies of formation of oxygen ring compounds (these assignments are mainly on the strength of data on one compound per ring structure). He did not assign ring corrections for entropies and heat capacities since the relevant data did not exist. The corrections used in reference 18 were made on the basis of estimating entropy changes associated with cyclization of aliphatic systems. The data base will be expanded with our data on chroman, isochroman, 2,3-benzofuran, 4,5-dihydro-2,3-benzofuran, and planned studies on 2,5-dihydro-3,4-benzofuran and xanthene. However, other key compounds with the oxygen atom in specified positions are required to obtain a wide ranging group additivity scheme for oxygen ring systems.

Nitrogen Compounds

Of all the classes of organic compounds the nitrogen compounds and particularly the multi-ring heteroaromatic nitrogen compounds are the most in need of additional study. For the straight-chain aliphatic amines existing, experimental data and statistical mechanical calculations should suffice as a data base for an estimation scheme. Some study into buttressing effects present in branched amines should be done. An excellent data base for molecules containing pyridine-like structures is now available with completion of our studies on the dimethylpyridines (21). This work combined with earlier

studies on pyridine and the methylpyridines will also provide an excellent data base to account for methyl group contributions. Significant progress has been made for multi-ring systems with completion of studies on quinoline, isoquinoline, acridine, and phenanthridine (3,4-benzoquinoline) in this laboratory. Because the nitrogen is so intimately involved in the aromaticity of these systems, it is important to investigate the effect of interactions between the aromatic nitrogen and its non-nearest neighbors. The Benson scheme ignores these effects. Planned studies on 5,6-, 6,7-, and 7,8-benzoquinoline will address this question. Also, 7,8-benzoquinoline data will provide the means to derive an important group contribution unavailable from any other data source.

Earlier work at NIPER (22) on additivity in pyrrolic systems reached the conclusion that they could not be calculated by the present additivity methods. These compounds are very important in the processing of the alternate crudes (see chapter 8), and their thermochemical properties calculation is a necessity. A widening of the data base is required to include substituted pyrroles, benzopyrroles, and carbazoles.

Partially hydrogenated aromatic nitrogen heterocyclic compounds have not been studied thermochemically in modern times other than at NIPER. A basic key compound data set is required to make group additivity assignments, and such measurements have formed part of our program to date. The attainment of thermochemical data on the partial hydrogenated quinolines will give insight into the conditions required for removal of the nitrogen atom without complete hydrogenation of the ring system (see chapter 4).

Sulfur Compounds

The thermodynamic study of the sulfur compounds present in light crudes was undertaken at NIPER in the period 1950-70 with the accumulation of a lot of data used extensively in the petroleum industry at present. The heavier crudes and other fossil fuels contain even more sulfur than the light crudes. The range of sulfur compounds is also more extensive with sulfur bonded in 5- and 6- membered rings as well as thiols, sulfides, disulfides, sulfoxides, and sulfones.

Calculation of the thermochemical properties ($\Delta_f H^\circ$, S° , and C_p) in the gas phase for sulfur-containing organic molecules has a strong base of available data. However, polycyclic aromatic hydrocarbon systems with S substituents, e.g., 1- and 2-thianaphthalene, have never been studied. Earlier studies have shown a relationship between O- and S-substituted 5-membered ring systems in calculating gas phase enthalpies for formation, but similar relationships for the entropies and heat capacities require further heat capacity measurements. Studies on key ring structures are required to widen the data base to include structures present in the future crudes.

Multi-heteroatom Compounds

Studies on ring systems containing more than one heteroatom are scarce, and a data base needs to be built. Measurements need to be made on key compounds to describe the prevalent compounds of this nature found in the alternate crudes.

Organometallic Compounds

Petroleum, shale oil, tar sands, and coal contain a range of metals and nonmetals which hamper processing. Among the main problems are compounds of Fe, V, Ni, Ti, and As. The thermochemistry of organometallics is still in its infancy with the methodology as yet not devised for the study of a number of metals including all the above. The field requires innovative breakthroughs and measurements made on selected organometallics. Success in this field will require extensive knowledge of basic inorganic and organic chemistry as well as thermochemical expertise. An example of just such innovation was the initial rotating bomb combustion calorimetric study of an organosilicon compound made by Good et al. (23) here at NIPER. The methodology devised made combustion calorimetric measurement of organosilicon compounds possible and helped define the standard enthalpy of formation of SiO_2 , the key being combustion with a fluorine additive having H_2SiF_6 as a final solution in excess HF, whereas previous combustions were unsuccessful due to SiO_2 being a near perfect fire retardant.

At present, most of the thermochemical data in the field is tentative and may be in error by an enormous amount. Earlier work again here at NIPER on tetraalkyl lead compounds showed errors of several 100 percent in previous literature enthalpies of formation (24). Further details of organometallic thermochemistry are given in references 25-27.

Measurements of heat capacities and entropies for organometallic compounds are very rare. With the exception of very stable, easily prepared compounds, such as ferrocene, one can say these measurements are nonexistent at present. Reasons for obtaining a strong data base in this area are given throughout this reassessment.

Vapor Pressure and Enthalpies of Vaporization/Sublimation

The conversion of condensed phase thermochemical data to the ideal gaseous state requires accurate measurements of the vapor pressure of the compound, or direct measurement of its enthalpy of vaporization/sublimation over the temperature range of the measurements. Vapor pressure data over a suitable temperature range can be used with the Clapeyron equation to calculate enthalpies of vaporization/sublimation within the given temperature span. However, direct measurement of the enthalpy of vaporization/sublimation experimentally is to be preferred where possible. In a suitable apparatus, measurements of vapor heat capacities of the real gas are also possible in combination with the enthalpies of vaporization (28). These measurements also give important information about the state properties of the gas in the region of low relative temperature and pressure; e.g., values of B_v , the second virial coefficient (28).

Appendix 7.2 lists the available tabulations of critically evaluated vapor pressure data on organic compounds. Numerous equations have been proposed for representing the vapor pressure data on chemical substances. It seems no one equation for fitting the vapor pressure data on all substances with high accuracy has found universal acceptance among investigators. In the past, mathematically simple equations were used and adjustable parameters found by simple graphical and numerical methods. With the advent of computers the complexity of the equations increased. No one equation, however, has been found that will fit the vapor pressure curves for all chemical substances over the entire temperature range from the low temperature triple point up to the

critical point. Early compilations have adopted the Antoine equation for representing the vapor pressure data on many classes of hydrocarbons and related compounds found in petroleum. With recent improvements in vapor pressure measurements, the results obtained have greater precision, accuracy, and wider temperature range. Consequently, better vapor pressure equations are needed to represent the experimental measurements. Scott and Osborn (29) chose five simple vapor pressure equations for fitting vapor pressure of several typical chemical compounds. From the results obtained, they concluded that the Cox equation yielded by far the best extrapolation both to lower and higher temperatures. However, several other equations are in general use, and new ones are being proposed. The above indicates the complexity and confusion involved in choosing an appropriate vapor pressure equation for representing the vapor pressure of chemical compounds. Similar confusion exists in the calculation of enthalpies of vaporization from the vapor pressure data via the Clapeyron equation.

Since none of the equations (including the Cox equation) would be expected to extrapolate reliably to high temperatures up to the critical point, it is important that vapor pressure measurements should be made over the widest possible temperature range. Most of the compounds of interest decompose before their critical temperature, and long residence times at high temperatures are also detrimental. This means that new rapid but accurate methods of vapor pressure measurements are required. For higher molecular weight compounds the vapor pressure at room temperature is low, but enthalpies and entropies of vaporization at 298.15 K are required for the present group contribution schemes calculating enthalpies of formation at 298.15 K in the gas phase. Possibly a more overriding reason for vapor pressures at 298.15 K is for specifying volatilities for environmental and health requirements. New methodology for the measurement of low vapor pressures and improvement of the present effusion methods are therefore of critical importance. The experimental goals in vapor pressure measurements can be summarized as: (1) measurements over as large a temperature range as possible, (2) measurements made as rapidly as possible without sacrificing the precision or accuracy, and (3) measurements made to as low a pressure as possible.

With the confusion and complexity in the experimental side of vapor pressure measurement being so great, it is no surprise that in the estimation side the field is equally confusing. To use a colloquium "estimation methods

for vapor pressures and enthalpies of vaporization are two a penny." It can be said that none of generalized vapor pressure correlations is very accurate for aromatic compounds, heteroatom-containing compounds, or situations where intramolecular forces are strong. Among the most promising recent methods for estimation of vapor pressures are those outlined by Ambrose (30) and Kobayashi (31). Group contribution schemes for estimation of enthalpies of vaporization at 298.15 K have been outlined by various groups, notably references 32 and 33. However, the lack of data on compounds other than alkanes precludes choices of group parameters. Harg, in her paper "Shortcomings in Physical Property Correlations - An Industrial View" (34), notes that "the group contribution methods are becoming increasingly important in the estimation of pure component properties." The extension of programs like CHETAH (16) to include group contributions for vapor pressure and enthalpies of vaporization should be a goal. This would require a new assessment of the available vapor pressure/enthalpy of vaporization data and not a rehash of present group values. Correlations to date have used all the available data without regard to its accuracy or precision. Also, a scheme applicable to just 298.15 K will be of little value to chemical engineers; as wide a temperature range as possible is required.

The pure compound vapor pressure data forms the base for any correlation used by petroleum engineers to estimate vapor pressure/temperature relationships for crude fractions. The lack of data on polycyclic aromatic hydrocarbons and heteroatom compounds have made such correlations, i.e., coal liquids, at best inaccurate. The need for data on a range of such compounds is well reported in the literature and is exemplified by the paper by Zudkevitch, Krautheim, and Gaydos (35) on the vapor pressure of coal-liquid fractions. In this area (petroleum engineering correlations), close cooperation between the correlators and those making measurements is required so that the "right" key compounds are studied and available data is properly assessed for accuracy and precision.

Standard States

Thermochemical measurements are related to a standard state of 298.15 K and 1 bar pressure. As noted above, as the molecular weight of the compounds to be studied increases the vapor pressure at 298.15 K decreases, and its

accurate measurement becomes more difficult, if not impossible. The common group additivity schemes, however, are centered around the thermodynamic data at 298.15 K. There is a good argument to be made to shift the standard state to a higher temperature, say 400 K or higher, where accurate vapor pressure measurements are possible on the high molecular weight components of heavy petroleum, shale oil, tar sands, and coal liquids. Also, the importance of obtaining group contributions as a function of temperature and not just at 298.15 K is obvious. The reassessment of the group contribution scheme outlined above should be made in such a way that it is applicable over as wide a temperature range as practicable. This is where the results from statistical thermodynamics will make a large impact on the setting up of a wide ranging group additivity scheme capable of calculation of both thermophysical and thermochemical properties of a range of compounds present in the alternate feedstocks.

Statistical Thermodynamics

In this section we will examine the current state of thermodynamic calculation of thermal properties for organic compounds in the vapor phase. We will provide a brief summary of present capabilities in the field, the data accumulated over years of research, and examine noticeable gaps and deficiencies in the accumulated data base.

To accomplish this task, the discussion was split into three topics: state of the science of determining thermodynamic properties of organic compounds in the vapor phase, current state of the available thermodynamic data, and deficiencies in this data base.

State of the Science

A brief explanation of a statistical thermodynamic calculation of thermal properties is required first. One major goal of thermodynamics is the prediction of possible chemical reactions. Practical implications of this are obvious. The Gibbs free energy content of the reacting and reactant molecules are needed to predict the reaction possibility. To determine the free energies, the enthalpy, the entropy, and heat capacity thermodynamic functions are needed. All of these thermodynamic functions can be calculated from the molecular partition function, provided the compound is in a low

pressure gaseous state. Thus, if one wishes to predict chemical reactions in the vapor state, only vapor phase Gibbs free energies are required. So, ultimately, if one knows the molecular partition function of a molecule, all of the thermodynamic functions can be calculated, and possible chemical reactions can be predicted.

Several parameters are needed to calculate the the molecular partition function and the resulting thermodynamic functions. These are: the moment of inertia, the molecular weight, the symmetry number, and the fundamental vibrational frequencies. Except for the vibrational frequencies all of these are easily determined.

A molecular vibration is described as any motion of the atoms within a molecule such that the atoms move only in relation to each other. For a nonlinear molecule with N atoms, there are $3N-6$ fundamental vibrations with each one having its own characteristic vibrational frequency. Thus, any vibration of the molecule can be described by a combination of these fundamental vibrations. All $3N-6$ frequencies are required for a statistical thermodynamic calculation. Unfortunately, these frequencies are usually the most difficult parameters to obtain.

To include these frequencies, both infrared and Raman spectra are collected using the appropriate instrumentation. By carefully analyzing these spectra, most of the $3N-6$ frequencies can be found. To verify the discovered fundamental frequencies and fill in those not found, a mathematical procedure called normal coordinate analysis is often employed. So, not surprisingly, the calculation of thermodynamic properties of molecules in the vapor state is more a spectroscopic than a thermodynamic problem.

Each molecule has its own set of unique fundamental frequencies. Therefore, the process must be repeated for each molecule. Since the number of fundamental vibrational frequencies expected rises at three times the number of atoms in the molecule, it follows that for large molecules the calculation can become challenging and slow. With present experimental and mathematical procedures, it can be extremely difficult to calculate the thermal gas properties for very large molecules.

But what types of molecules are approachable with statistical thermodynamic calculations? Atoms, diatomic molecules, and other very small

molecules are easily calculated with statistical thermodynamic calculations. The majority of these molecules have their thermal properties calculated. Indeed, their properties can be calculated much faster and more accurately than they can be measured (36). The widespread use of the JANAF tables illustrates the success of small molecular thermal calculations.

The next step in complexity involves molecules ranging from 5-12 atoms. These molecules generally are treated quite adequately provided they are not long chain hydrocarbons. The bulk of the available thermodynamic data involves molecules in this range.

Molecules over 12 atoms comprise the next level of complexity and can range from moderately to extremely difficult. Usually, rigid molecules which do not have components that rotate with respect to the rest of the molecule are the best suited for measurement. These types of rotations are called internal rotations, and generally two to three internal rotations can be handled accurately.

For molecules with long flexible chains and many internal rotations, several estimation procedures have been developed that yield satisfactory answers. These methods employ significant approximations to statistical thermodynamic calculations or depend heavily on data from more theoretically rigorous statistical thermodynamic calculations. Structural similarities and group contributions are used to estimate the needed thermodynamic data (23).

In summary, large rigid molecules with up to 25 atoms, and possibly many more, can be treated accurately with statistical thermodynamic calculations, but flexible long chain type molecules present serious problems. For these long chain-like molecules, group contribution methods are often used but still rely heavily on the data obtained from simpler molecules using statistical thermodynamic calculations.

Current State of Gas Phase Thermodynamic Data

The available data for gas state thermodynamic functions is somewhat scattered. Rather than attempt an exhaustive review only the most prominent sources will be mentioned. For atoms, diatomics, and other small molecules the JANAF tables (38) are the definitive source and cover a wide selection of these molecules.

For moderate to large molecules, the data is spread among the published chemical literature. Perhaps the most complete compilation and extension of the available ideal gas thermodynamic data is the publication of Stull, Westrum, and Sinke (39) on "The Thermodynamics of Organic Compounds." The ideal gas thermodynamic data from 298 to 1000 K are tabulated for 918 compounds.

Another source for data on "key" compounds is the American Petroleum Institute's Monograph Series (40). The data tabulated in these monographs is either gathered directly from journal articles or calculated and estimated in-house.

Using these sources we can list the molecular compound types that have tabulated thermodynamic data. Data exist for the alkanes, alkenes, alkydienes, alkynes, cycloalkanes, cycloalkenes, and alkylcycloalkanes. The alkanes have data on molecules up to 10 carbon atoms over a variety of branched and straight chain species, with a smaller listing of molecules to 20 carbon atoms or more. The remaining hydrocarbons generally have no data after 10 carbon atoms in size. The bulk of this data relies heavily on fitted estimation methods.

The aromatic compounds are considerably less documented. The majority of aromatic compound data is centered in the methyl- and ethylbenzenes. The only polycyclic aromatic compounds tabulated, outside a few tabulations in the API monograph series, are the alkylnaphthalenes. Interestingly, the only spectroscopic determination in this series is naphthalene. The rest are found by group contribution methods using the data collected on the alkylbenzenes. Thus, data for 21 molecules were determined from the spectroscopically determined thermodynamics of naphthalene. This demonstrates the large economy achieved in building a thermodynamic data base using the key molecule approach.

For the oxygenated compounds, the thermodynamic data base is similar to the hydrocarbons, but much smaller with a general upper carbon number of 6 for the molecular size. The smaller ethers, aldehydes, ketones, and alcohols analogous to the hydrocarbon alkanes are listed. The number of aromatic compounds containing oxygen which have published gas phase thermodynamic data is extremely small. Only a few phenols and carboxylic acids are listed.

The nitrogen compound data is focused primarily on the alkylamines with some nitro and nitrile compounds also being tabulated. A few cyclic nitrogen-based aromatics are listed. Most of these are based on work accomplished in Bartlesville.

The data for halogenated compounds are based on the halogenated hydrocarbons and the halogenated benzene derivatives. Most of these compounds are quite small and rarely exceed a few carbon atoms in size.

The sulfur compounds are represented better than the nitrogen and oxygenated compounds. Research of the Bureau of Mines at Bartlesville produced the data for the majority of the sulfur compounds listed. The mono and dithiaalkanes, thiacycloalkanes, and various thiols are represented. The only sulfur heterocyclic compound listed is thiophene.

Deficiencies in Current Available Ideal Gas Thermodynamic Data

The deficiencies in the available data base can be divided into two types: a lack in range of molecular weight, and a lack of specific key molecules.

In the compound types previously addressed, the oxygen and nitrogen-based compounds are the most severely lacking in adequate thermodynamic data. Cyclic molecules of even moderate size are totally missing. Much of the lack has been due to that of developed spectroscopic techniques to examine the molecules, but recent advances in computing technology and IR/Raman instrumentation have placed the molecules within experimental reach.

The other major data base deficiency lies in extending the compounds to polycyclic molecules. As noted in previous sections, these molecules are spectroscopically "difficult" molecules, but the difficulties are not insurmountable. The rewards and data base increase are enormous. The naphthalene example cited earlier is a good example. Here the data for one key molecule were expanded by estimation techniques to 22 molecules. Stull et al. (39) point out that their tabulated data of 118 sulfur compounds were estimated from accurate statistical thermodynamic calculation of approximately 20 "key" compounds. They imply that the data base extrapolation could be extended much further.

Except for projects funded by the American Petroleum Institute and the JANAF tables, very little is being done to expand the data base or fill in glaring deficiencies.

To fill these gaps the following procedure is proposed as a possible guideline for directing the NIPER spectroscopy lab efforts. First, the "key" molecules needed to fill the ideal gas thermodynamic data base deficiencies are identified. Then, those key molecules most amenable to investigation are chosen for investigation. Next, the experimental thermodynamic functions are determined and the spectroscopically calculated thermodynamic functions are calculated. In addition, new computational methods for calculating the ideal gas thermodynamic functions are tried for possible future use. Then, the results of these investigations are compared and necessary corrections and adjustments are made. Using the spectroscopic results, the gas phase thermodynamic functions are extended to industrial processing temperatures. Lastly, these results are used to expand the existing thermodynamic data base using various estimation techniques, and new key molecules are identified. At this time few, if any, research facilities, excluding the NIPER Thermodynamics Research Group, have the equipment or manpower to support simultaneous experimental and spectroscopic thermodynamic measurements. The chances of developing a reliable gas phase thermodynamic data base, without correlating spectroscopically and experimentally determined thermodynamic data, are slim.

Three areas of modern statistical thermodynamic calculation of gas phase thermal data were examined. The current experimental methodology and capabilities were discussed. We concluded that rigid molecules up to 25 atoms, or possibly more, can be accurately handled. Semiflexible molecules of this size may be handled by various estimation methods. The gaseous thermal data base contains many deficiencies that need to be rectified before many useful industrial calculations can be made. These deficiencies are most pronounced in the oxygenated and nitrogenated compounds. Lastly, it was concluded that a twofold approach of experimentally and statistically thermodynamically determined thermodynamic data is needed to fill these database deficiencies.

Semi-Empirical Calculations

Application of the "correction terms" in group additivity bond enthalpy schemes requires chemical intuition and is not foolproof. Failure to allow for all the interactions can lead to serious errors, and it is difficult to assure that all possible ones have been included. The advent of empirical molecular mechanics force field calculations which can determine energies of molecules along with structures and other properties have added a new dimension to the estimation field. The "correction terms" are calculated using the force field and added to a group contribution scheme to give an overall enthalpy of formation in the gas phase. A number of these force fields (41) have been described in the literature in the last 20 years or so with Norman L. Allinger being a leader in the field. However, the force field method has been applied to date with success only to a few compound types with most discussion limited to alkanes and acyclic hydrocarbons. Recent innovations have expanded the molecular mechanics method to benzoidal-type hydrocarbon systems, but as yet few or no heteroatom-type compounds have been included. A handicap of the molecular mechanics method (or, for that matter, any additivity scheme) lies in the fact that it is an empirical method; hence, a great amount of accurate data must be available for a given class of compound before an appropriate force field can be developed. A second handicap of the molecular mechanics method is the necessity for accurate structural data on the basic set of compounds used to derive the force field. However, the methodology holds promise as a new and innovative method of obtaining thermodynamic data on a range of compounds when the data base on appropriate key molecules is available.

When operating in an ideal case, the molecular mechanics computer program will be capable of producing complete thermodynamic functions for the given molecule. At present no such program exists, and the individual ones either calculate vibrational spectra and the related thermodynamic functions, e.g., C_p and S° , or calculate enthalpies of formation and structure in the gas phase.

Application of the molecular mechanics methodology to alcohols and ethers (42), amines (43), sulfides and thiols (44), and, more recently, systems containing $C_{sp^2}-S$ (excluding $\Delta_f H^\circ$ values) (45) have shown the potential of this type of computer-based calculation.

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Appendix 7.1

Sources of Thermochemical Data

The following is a listing of the sources of critically evaluated thermochemical data leading to the Gibbs free energies of inorganic and organic substances. Publications like handbooks are not included.

- o CODATA Recommended Key Values for Thermodynamics. CODATA Bulletin No. 28 1977.
- o Selected Thermochemical Data Compatible With the CODATA Recommendations. NBS publication almost entirely inorganic.
- o NBS Tables of Chemical Thermodynamic Properties. Published in J. Phy. Chem. Ref. Data, v. 11, Supplement 2, 1982. This replaces NBS Technical Notes 270, 1-8.
- o Thermal Constants for Substances (Termicheskie Konstanty Veshchestv). Russian counterpart of NBS Technical Notes 270.
- o JANAF Thermochemical Tables. Latest supplement in J. Phy. Chem. Ref. Data, v. 11, 1982, pp. 695-940.
- o Selected Values of Chemical Thermodynamic Properties. Circular 500.
- o Selected Values of Properties of Hydrocarbons and Related Compounds. Produced by Thermodynamics Research Center (TRC) Texas A&M University; these tables are a continuation of Circular 500 and API Project 44 tables.
- o Key Chemical Data Books. Published by TRC Texas A&M. Compounds for which data have been correlated include phenol, benzene, cresols, xylenols, furan, dihydrofuran, and tetrahydrofuran.
- o API Monograph Series. Published by American Petroleum Institute these monographs are on compounds present in synfuels. To date, monographs API 705 to API 716 have been published.
- o The Chemical Thermodynamics of Organic Compounds. D. R. Stull, E. F. Westrum, Jr., G. C. Sinke, Wiley, New York, 1969. This monograph deals with the thermochemical properties of 918 organic compounds in the ideal gas state from 298.15 K to 1000 K.
- o Thermochemistry of Organic and Organometallic Compounds. J. D. Cox and G. Pilcher, Academic Press, 1970. Critical compilation of enthalpies of formation with estimates of experimental error for some 3,000 substances in both gaseous and condensed states.
- o Sussex-NPL Computer Analyzed Thermochemical Data. Organic and Organometallic Compounds, J. B. Pedley and J. Rylance, University of Sussex, England, 1977. Updated version of Cox and Pilcher produced by computer analysis.

- o Selected Values of Heats of Combustion and Heat of Formation of Organic Compounds Containing Elements C, H, N, O, P, and S. E. S. Domalski, J. Phys. Chem. Ref. Data, v. 1, 1972, pp. 221-77.
- o Thermodynamic Properties of Key Organic Oxygen Compounds in the Carbon Range C₁ to C₄. R. C. Wilhoit, J. Chao, K. R. Hall, J. Phys. Chem. Ref. Data, v. 14, 1985, pp. 1-175.

This list is not complete, and further references can be found in the CODATA Bulletin No. 55, April 1984, on Chemical Thermodynamics edited by R. D. Freeman. The Journal Physical Chemistry Reference Data will continue to be a major source of critically assessed data in all fields of thermodynamics.

Appendix 7.2

Vapor Pressure Data

The following is a listing of the major sources of critically evaluated vapor pressure data, handbooks are not included.

- o Vapor Pressure of Pure Substances, Organic Compounds. D. R. Stull, Ind. Eng. Chem., v. 39, 1947, pp. 517-40. This dated compilation is still the major source of data for handbooks containing data on 1,200 organic compounds. Almost 25 percent of the data dates from pre-1900.
- o Vapor Pressure of Organic Compounds. T. E. Jordan, Wiley Interscience, 1954.
- o Circular 500 and TRC Publications. See appendix 7.1.
- o The Vapor Pressure of Pure Substances. T. Bailblik, V. Fried, E. Hala. Elsevier, Amsterdam, 1973.
- o Computer-Aided Data Book of Vapor Pressure. S. Ohe, Data Book Publ. Co. Tokyo, Japan, 1976.
- o Antoine Vapor Pressure Constants for Pure Compounds. I. Wichterle, J. Linek, Prauje, 1971 (in Czech).
- o Physico-Chemical Constants of Pure Organic Compounds. J. Timmermans, Elsevier Publications, Amsterdam, v. 1, 1950; v. 2, 1965.
- o Vapor Pressure of Coal Chemicals. J. Chao, C. T. Lin, T. H. Chung, J. Phys. Chem. Ref. Data, v. 12, 1983, pp. 1033-63.
- o Enthalpies of Vaporization of Organic Compounds a Critical Review and Data Compilation. Editors V. Mayer, V. Svobado, IUPAC Chemical Data Series No. 32, Pergamon Press, London, 1985.
- o The TRC Thermophysical Property Data File 1. Vapor Pressure. An online compilation available from Technical Data Base Services, Inc., New York.

Further references can be found in the CODATA Bulletin No. 55, April 1984, on Chemical Thermodynamics, edited by R. D. Freeman. Other sources of data can also be found in the bibliography in the paper by Chao, Lin, and Chung.

8. COMPOUND SYNTHESIS AND PURIFICATION

An important part of all thermodynamic studies is the attainment of pure compounds. Accurate and precise measurements of thermodynamic properties require pure samples of the compounds under study. Small amounts of impurity in a sample can lead to grossly erroneous results; e.g., the presence of 0.1 percent of water in a sample of anthracene in combustion calorimetry would lead to an error of 5.5 percent on its standard enthalpy of formation if measurements were made on the basis of mass of sample burned. Basing the results on CO₂ analyses would correct for this error, but in other thermodynamic measurements on the sample, this type of correction is not possible. Sample purities are normally given in terms of number of 9's; e.g., one (90 percent), two (99 percent), three (99.9 percent). In thermochemical measurements (enthalpies of combustion, condensed phase heat capacity, and vapor pressure measurements), purity requirements are normally at least three 9's, and preferably four 9's. In PVT measurements, four or five 9's are required.

The synthesis and purification group at Oklahoma State University (OSU) led by Professor E. J. Eisenbraun has been the source of many of the compounds studied at NIPER in recent years. The synthesis and purification of compounds by a central group such as the one at OSU prevents large-scale duplication of effort, uses the great amount of synthetic organic chemistry expertise gathered by the group over the years, and leaves the thermodynamicists free to make measurements. The synthetic organic chemistry literature is growing at an enormous rate, and many compounds can be prepared in high yields using organic reagents unknown just a few years ago. It is highly inefficient to have thermodynamicists try to make the compounds, purify them, and also make the measurements.

In the past, the API Projects 44, 52, and 60 supported research on the synthesis, purification, and properties of hydrocarbons and related substances that produced a large number of chemical compounds which comprised the most complete source in the world of very high purity reference standards. These ultra-high purity chemicals are still used for the calibration and testing of instruments and methods of measurement of many kinds of spectroscopic and

physical properties. API standards are invaluable for calibration of gas chromatographs and in high pressure liquid chromatographic analysis (HPLC). We anticipate the continued supply of such samples from the OSU laboratories as a valuable aside to the production of compounds for thermodynamic studies.

9. DIFFERENCES BETWEEN LIGHT PETROLEUM AND OTHER FOSSIL FUELS

As already noted earlier, it will never be possible to measure all the needed properties on all of the mixtures that may be encountered in synthetic fuels. In petroleum, industry experts have found that the properties of undefined mixtures have been accurately simulated by representing the system as a mixture of carefully selected pure compounds whose thermodynamic and physical properties are accurately known. Extension of this method is what is required now. Work on pure components of molecular types found in heavy petroleum, shale oil, coal, and tar sands or closely related analogies will define a base for estimation of the properties of unmeasured compounds. The choice of the key compounds is a cornerstone to the successful operation of the whole scheme. Close cooperation between the experimentalists and those attempting the correlations is required to keep the direction of the studies on line and within reasonable bounds. A complete selection of pure compounds cannot, and should not, be made at the start of such a comprehensive study. Such rigidity would prevent necessary interaction and follow up of promising new processes. The next sections highlight the major differences between materials derived from light petroleum and heavy petroleum, shale oils, coal, and tar sands. These differences will help in the choice of the key compounds for study.

Heavy Petroleum

Most molecules in petroleum heavy ends contain 20 to 40 percent aliphatic groups substituted to aromatic or heteroaromatic rings (1). These aliphatic groups are:

- o normal and isoalkyl groups (C_2 to C_{16}),
- o cycloalkyl groups (usually C_5 or C_6), and
- o methylene groups linking two aromatic rings.

Table 9.1 gives representative structures for the aromatic ring systems present in heavy petroleum.

Problem compounds affecting the economics of processing heavy petroleum include those containing heteroatoms. Tables 9.2 to 9.4 give representative parent nitrogen-, oxygen-, and sulfur-containing compounds which occur in

heavy petroleum crudes. These compounds also occur with normal or isoalkyl substituents. In addition to the monoheteroatom aromatic compounds, various mixed heteroatom ring systems are also present. Table 9.5 gives some of the parent identities found. Further details on compound types can be found in references 2, 3 and 4.

Organic metal complexes occur in heavy petroleums, their amount increasing with the boiling point of the oil. Complexes of vanadium, nickel, copper and iron are present in both porphyrin and nonporphyrin type structures. Typical structural types are given in table 9.6 (5).

Shale Oils

Shale oil, and in particular oil derived by pyrolysis of the shale, typically has a much higher content of olefins, and nitrogen-, oxygen-, and (to a lesser extent) sulfur-containing compounds than petroleum. The presence of 1-, 2-, and 3-alkenes and olefin substituted aromatic compounds, e.g., α -methylvinyl naphthalene, is a significant difference from light petroleum (6). Most of the heteroatom compound types given in tables 9.2 to 9.5 as being present in heavy petroleum are also present in shale oils. In shale oil the relatively large nitrogen content makes the nitrogen heteroaromatic compounds of particular importance. The presence of aliphatic nitriles (up to C₃₄), methyl ketones, and amides are additional features of shale oils. References 7 to 10 give some details of compound types found in shale oils.

TABLE 9.1. Some aromatic ring systems present in heavy petroleum

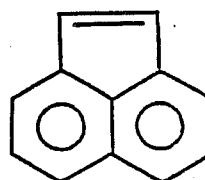
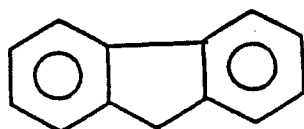
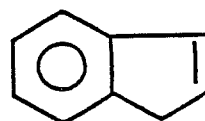
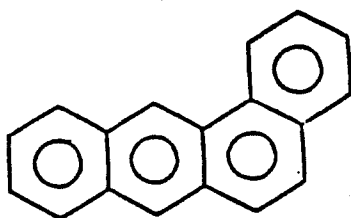
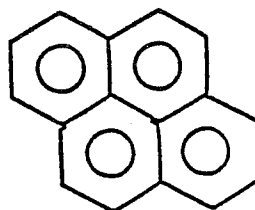
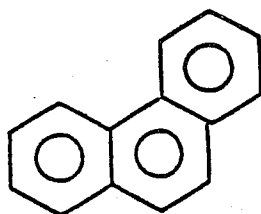
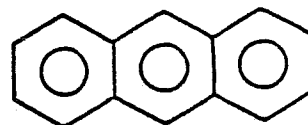
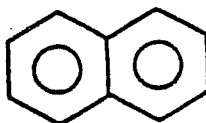
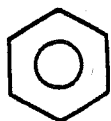


TABLE 9.2. Representative nitrogen-containing compounds
in petroleum crudes

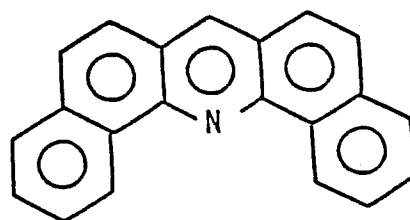
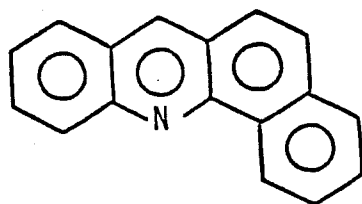
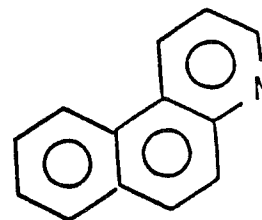
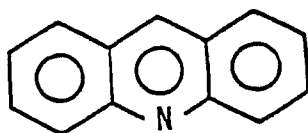
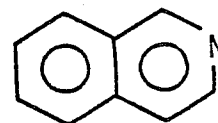
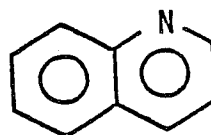
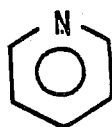
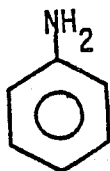
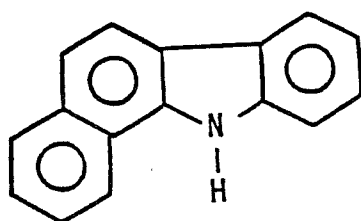
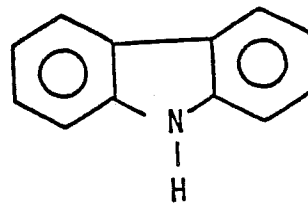
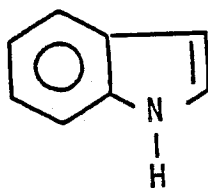
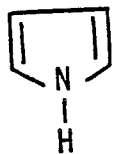


TABLE 9.3. Representative oxygen-containing compounds
present in heavy petroleum

R-COOH

where R = aliphatic or aromatic group

R-O-R

R-OH

where R = group such as indanyl, naphtho, etc.

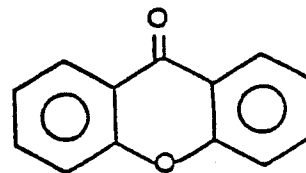
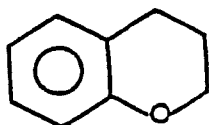
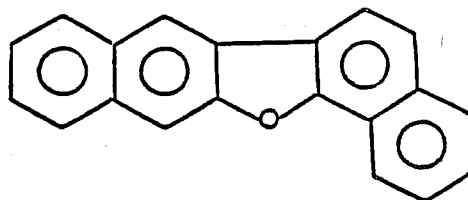
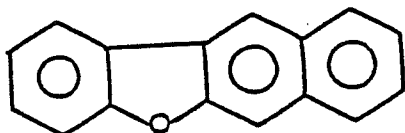
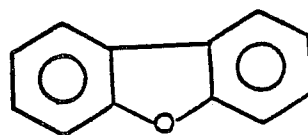
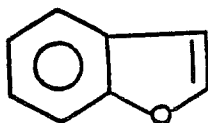
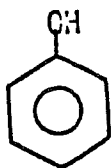
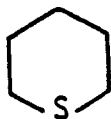


TABLE 9.4. Representative sulfur-containing compounds
in petroleum crudes

R-SH



R-S-R¹



R-S-S-R¹

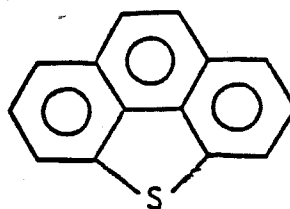
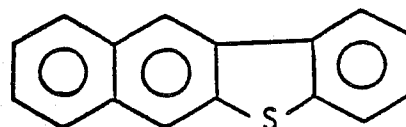
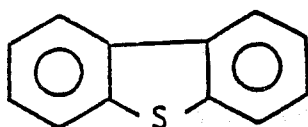
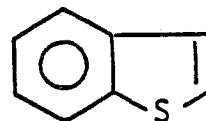


TABLE 9.5. Some representative diheteroatom compounds present in heavy petroleum

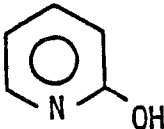
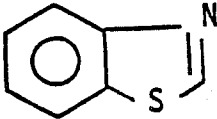
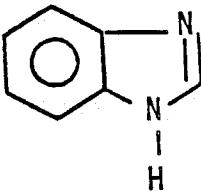
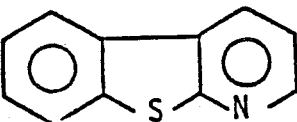
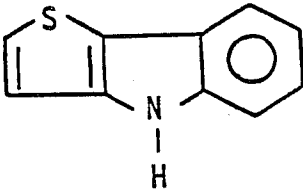
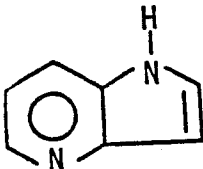
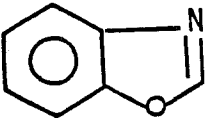
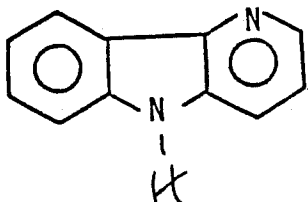
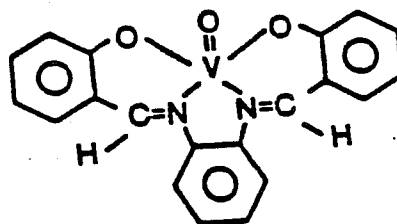
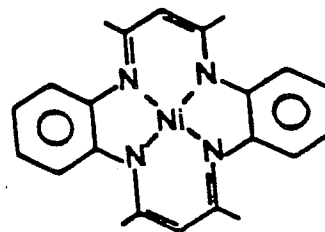
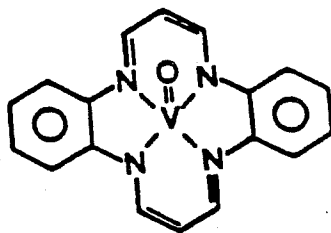
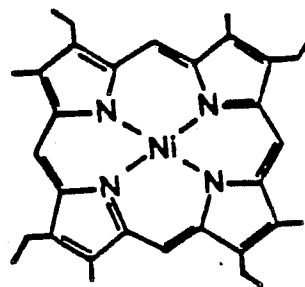
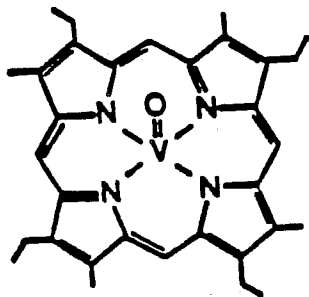
R-SO-R	R-SO ₂ -R	
		
		
		

TABLE 9.6. Possible vanadyl and nickel porphyrin and non-porphyrin compounds found in heavy petroleum



Coal Liquids

Two major changes between sweet light petroleum and coal liquids are the lower hydrogen content of the latter and its high oxygen content. Table 9.7 compares typical weight-percent analyses for carbon, hydrogen, oxygen, nitrogen, and sulfur for petroleum, raw shale oil, tar sands, and coal. The coal structure contains more polycyclic aromatic hydrocarbons than either heavy petroleum or shale oil. The high oxygen content means that the relative importance of phenolic, carboxylic acid, and ether-linkage-containing compounds increases when considering coal liquids. Table 9.8 lists some probable oxygen-containing compound types present in coal liquids. The range of nitrogen- and sulfur-containing compounds discussed above as being present in shale oil and heavy petroleum also occurs in the coal liquids.

New models for coal structure are appearing at regular intervals in the literature. Of interest is one described by Professor J. W. Larsen at the 1985 ACS Division of Fuel Chemistry Meeting in Chicago (12). A structure for Illinois No. 6 coal proposed by Larsen is macromolecular. The composition of the model $C_{100}H_{84}O_{11}S_{1.8}N_{1.4}$ has five hydroxyl groups per 100 atoms of carbon. The extractable material that is not bonded to the network has an average molecular weight of 900. The number average molecular weight between crosslinks is 3000. Larsen thinks the startling feature of the model is the large number of active hydrogen bond crosslinks in the structural network. In this particular coal, the hydrogen bonds exceed the covalent links by a factor of four! Other coals may have different values.

Tar Sands

Bitumen extracted from tar sands by the hot water extraction process differs from each of the above fossil fuels in that it is highly viscous and very refractory. Like coal, polycyclic aromatic hydrocarbons are a major constituent of tar sands. Although the nitrogen content does not differ appreciably from conventional feeds, the denitrification process has proven considerably more difficult.

Functional group multiplicity is also a feature of tar sands. On the average in a tar sand sample, 20-35 percent of the molecules contain no heteroatoms, while up to 40 percent contain two or more. In addition, three-fourths of all molecules contain one or more aromatic rings with an average of

about two to three condensed rings per molecule. This results in multiple interactions cumulating in strong intermolecular association (e.g., asphaltene formation) or adsorption (e.g., catalysts inhibition or poisoning) even though the individual interactions are probably no stronger than in smaller molecules. The underlying objective in tar sand upgrading should, therefore, be reduction of intermolecular association before applying extreme processing conditions which can cause condensation reactions.

Processed Fuel

In addition to the above differences between light petroleum and the various other fossil fuels giving insights into areas where thermodynamic data is required, new problem compounds arise in the actual processing of the fuels. Table 9.9 reproduced from reference 13 highlights this point in the hydrotreating of shale oils. Reference (14) details further studies on the fate of nitrogen compounds in hydrotreating shale oil, and reference (15) details changes in composition resulting from hydrotreating at different levels of severity on SRC-II coal-derived liquid.

In addition to studies on the various classes of compounds actually present in the fossil fuels, studies are also required on, for example, their partially hydrogenated derivatives.

TABLES 9.7. Typical weight percent analyses of fossil fuels

	Weight percent				
	Light petroleum	Heavy petroleum	Raw shale oil	Coal (Illinois No. 6)	Tar sands
Carbon	85	83	84	77	82
Hydrogen	12	10	12	6	10
Oxygen	--	1	1	10	2
Sulfur	3	6	1	5	5
Nitrogen	0.1	2	2	2	1

TABLE 9.8. Probable oxygen-containing compounds in coal

Phenols

Naphthols

Ethers

Acids

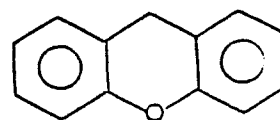
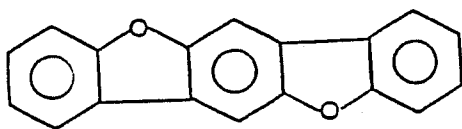
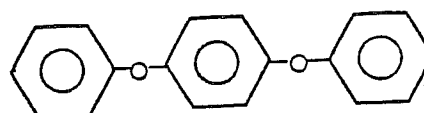
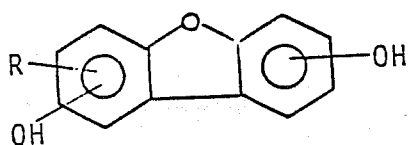
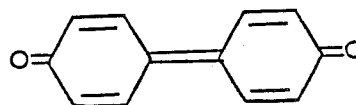
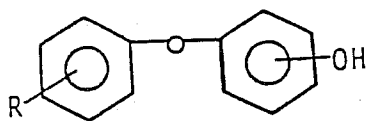


TABLE 9.9. Major chemical classes present in untreated and hydrotreated shale oils

Untreated Oil	Hydrotreated, Ni-Mo	Hydrotreated, Co-Mo	Hydrotreated, Ni-W
n-Alkanes (C ₇ -C ₃₅)	Small amount of cracking	Small amount of cracking	Relatively unaffected
Alkenes (1-, 2-, 3-enes)	Completely removed	Completely removed	Completely removed
Hydroaromatics, mainly indanes, tetralins	Significantly decreased	Significantly decreased	Significantly decreased
Diaromatics, mainly naphthalenes, (C ₁ -C ₆)	Significant cracking to C ₀ -C ₁ naphthalenes	Significant cracking to C ₀ -C ₂ naphthalenes	Significant cracking to C ₀ -C ₁ naphthalenes
Polyaromatics	Unaffected: more highly condensed material appears	Unaffected: more highly condensed material appears	Unaffected
Nitriles (C ₇ -C ₃₀), methyl ketones (C ₇ -C ₃₁)	Completely removed	Completely removed	Completely removed
Phenols (to C ₇), indanols (to C ₂), naphthols (to C ₆)	Significantly decreased	Significantly decreased	Relatively unaffected
Basic nitrogen compounds, pyridines (to C ₆), quinolines (to C ₃)	Significantly decreased	Significantly decreased	Some decrease
Basic nitrogen compounds, benzopyrroles, dibenzopyrroles (trace)	Some removal	Some removal	Some removal

^a Reproduced from reference 13.

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10. THERMODYNAMICS, KINETICS, AND CATALYSIS

Often thermodynamicists are told by industrialists, and even academics, that thermochemical data is irrelevant; kinetics govern everything. If they are talking about reactions at high temperature where thermodynamics predicts carbon to be the main product, then what they say is true; kinetics is the governing restriction. At lower temperatures, however, they are misinformed. In reality both thermochemical and kinetic data are equally important. Two of the major goals of physical chemistry are the prediction of equilibrium constants for chemical equilibria and the prediction of rate constants for "elementary reactions." In previous chapters we have discussed the thermochemical goal. Here we will attempt to discuss the kineticists' goal. First, an explanation of "elementary reactions" is required. Chemical reactions seldom occur as one concerted chemical event. Instead, they are composed of a series of what are termed "elementary steps." The series of such steps required to describe a chemical reaction is called the "mechanism" of the reaction. The goal of the chemical kineticist is to be able to predict the rates of these elementary steps, deduce the important steps participating in the overall process, and deduce a mathematical expression for the overall global reaction to produce products. The latter is what is called the "rate law." The problem is that, for many systems, the mechanism is so complex that it defies any simple effort to represent it in a series of steps in a closed form. The oxidation of methane, for example, is so complex that it involves 140 elementary steps. Such complicated systems are represented by a "model" if the rate constants are known.

Based on the transition state theory of elementary reactions, S. W. Benson has developed empirical methods for estimating rate constants. The methodology is outlined in his text "Thermochemical Kinetics" (1). In reading such texts it becomes obvious that the complexities of most reactions are so great that identification of major pathways is difficult, if not impossible, without guidance from thermochemistry. Mechanisms for free radical type reactions stand or fall on the measurements or estimations of bond dissociation energies and enthalpies of formation of parent molecules and their related radicals. Knowledge of thermochemical data on stable molecules and radicals has led to the great development in our understanding of chemical oxidation at the molecular level (2,3) which has occurred in recent years.

Benson, in his text, outlines methods, based on the thermochemical data of stable molecules, of calculating enthalpies of formation of transition states. This in turn leads to activation energies and activation entropies for possible reaction mechanisms. Physical organic chemists are also working along similar lines using molecular mechanics (force field) programs to calculate the thermochemical functions for "activated complexes" (4,5). Reference (5) gives a detailed account of the applications of molecular mechanics to the problems of the dynamics of chemical reactions.

The function of a catalyst--whether homogeneous or heterogeneous--is to increase the rate of a thermodynamically allowed reaction by lowering the activation energy barrier for the process.

Although the theory of heterogeneous catalysts has not advanced to the point where catalysts can be selected on a theoretical basis, the thermodynamic characteristics of catalytic substances and reactions are helpful in the selection of an appropriate catalyst. A catalyst will not work unless it has a chemical affinity for at least one of the reactants. It will also not work if the Gibbs free energy for the interaction of the catalyst with the reactant is larger than that for the reaction being catalyzed. Much effort has been expended in this field, but results are meager due to the problems of obtaining good thermochemical data for organometallic compounds (see chapter 6).

One example of catalyst selection via thermodynamics is that due to the work of Fahrenfort, van Reijen, and Sachtler (6) who studied the catalytic decomposition of formic acid. Platinum and palladium were the "best" catalysts on thermodynamic grounds, and subsequent work has proved the point. Similar work by Makishima, Yoneda, and Saito showed CuO and Cu₂O efficient catalysts for the oxidation of CO to CO₂ (7).

It is not adequate to consider thermodynamic requirements only in catalyst selection. Kinetic factors, types of electronic bonding, and matching the atomic geometry of the catalyst surface to the reactants and products are also important. Thus, catalytic activity depends on the method of preparation of the catalyst. Activity can vary on different faces of a single crystal. Activity can vary depending on the presence of promoters or modifiers. All these factors determine whether a thermodynamically accepted substance will become a real catalyst.

Schaefer (8) states that the fields of surface chemistry, organometallic chemistry, and heterogeneous catalysts all suffer from the lack of sufficient thermochemical and structural information. One of the tremendous strengths of organic chemistry is the existence of well-established and reliable values of bond energies and bond lengths for C-C bonds in different environments. In contrast, comparable information for transition metal to carbon bonds is rare. Skinner and Connor (9) have reviewed the field of metal-carbon bond energies in a recent plenary lecture. Ab-initio calculations (10) are one means of obtaining thermodynamic information, but again experimental numbers are needed. Beauchamp and co-workers (11) have measured particular metal-ligand bond energies as opposed to an average over several metal-ligand bond energies using an ion beam apparatus. Conventional calorimetry will generally yield only the average bond energy. Beauchamp's methodology is an exciting new field where the thermodynamicist, theoretician, and kineticist can all have an input to an overall understanding of catalysis.

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11. PREVIOUS SURVEYS OF THERMODYNAMIC DATA NEEDS

Most aspects of the problems of requiring research for fossil fuels discussed in this report have been the subject of earlier reports. In this chapter we draw the reader's attention to some of these reports; the list is not exhaustive. All reports are unanimous in establishing that the United States must make an effort to produce synthetic fuels and must attach great importance to the need for thermochemical and thermophysical data for the development of an efficient synthetic fuels industry. What follows is a brief reproduction of some particularly relevant statements from the reports or a brief summary of their context.

Conference on Thermodynamics and National Energy Problems

(Airlie House, Warrenton, Virginia, June 10-12, 1974)

This comprehensive energy systems report, containing sections on coal and "other fossil fuels," outlines the needs for thermodynamic analyses in a clear, concise form. It develops the idea of "key" compounds, kinds of experimental data required, and compounds to form the initial basis of such studies. The next three paragraphs summarize the main recommendations reproduced from the report summary.

The number of substances is estimated to be about 100 pure aromatic compounds and about 100 coal product mixtures. This will include a large number of methyl, sulfur, and nitrogen derivatives of the polycyclic compounds that have been found in coal products. Sample preparation, purification, characterization, spectroscopic and molecular studies, calorimetry up to 400° C, vapor pressure up to 500° C, viscosity, thermal conductivity, and diffusion coefficients and accurate biological assays should be included in an integrated program. Similar measurements on approximately 100 organic mixtures will be needed. A program of similar magnitude will be required for inorganic substances.

In the processing of natural petroleum and synthetic petroleum, to meet the current challenges, thermodynamic data are required principally on the following substances and properties.

Substances: Key compounds, hydrocarbons and related compounds, of higher molecular weight, C₁₀ and higher, including individual compounds of adequate high purity, and mixtures of them, carefully selected according to a model system.

Properties: Heats of formation, heat capacity, entropy, free energy, heats of fusion and vaporization, vapor pressures, densities, critical temperatures and pressures, and P-V-T data, over the appropriate ranges of temperature and pressure.

With the appropriate properties measured experimentally, with the necessary accuracy, on the selected "key" substances, with carefully chosen model systems, it becomes possible to develop correlation methods for calculating the properties of the many substances and mixtures that it will not be possible to measure directly.

Assessment of Technology for the Liquefaction for Coal

(Ad Hoc Panel on Liquefaction of Coal for the Committee
on Processing and Utilization of Fossil Fuels

National Academy Sciences, Washington, DC, 1977, FE/1216-3)

This report gives detailed comprehensive accounts of the technology for the liquefaction of coal. It includes technical and environmental evaluations. Although now somewhat dated, it gives clear, concise descriptions of the technology involved.

Assessment of Long-Term Research Needs for Coal-Liquefaction Technologies (FERWG-II)

(Fossil Energy Research Working Group
S.S. Penner, Chairman, March 1980)

We reproduce from the executive summary the following statements relevant to our report.

"Coal-liquefaction processes require an integrated systems approach in which all aspects of the technologies (coal preparation, hydrogenation, hydrogen production, bottoms processing, liquid refining, etc.) are properly considered and optimized."

We identify below important R&D areas, each of which we believe requires substantial additional funding (i.e., more than \$10⁶/year) and the first three of which we regard as especially urgent:

- o Research is needed on each of the following topics: the basic physics and chemistry, structure, composition, and thermochemistry of coals and of model compounds; volatilization; kinetics and mechanisms of bond scission; subsequent free radical and ionic reactions, including reaction steps involving unstable intermediates; transport properties and fluid mechanics of multiphase flows (see Section 2.1).
- o Fundamental and applied research should be pursued on separations of liquid streams and solids from the reaction products formed during coal liquefaction. These studies are needed in order to improve recycle systems to reduce processing costs. Vapor/liquid equilibria should be better defined, especially in regions near the critical points (see Sections 2.3, 2.4, and 2.5 as well as Appendix C).

Refining Synthetic Liquids from Coal and Shale

(Final report of the Panel on R&D Needs
in Refining of Coal and Shale Liquids,
National Academy of Engineering, 1980.)

The principal recommendation stated on p. 192, reads as follows:

RECOMMENDATIONS

Although refining processes capable of producing conventional fuels from oil and shale are available, high hydrogen consumption, poor selectivity, and, in some cases, low catalyst activity and life indicate the need for major improvements. The petroleum industry in the United States is capable of developing synthetic fuel refining processes and is carrying on a considerable amount of exploratory research, but the clearly distant need for major synthetic fuel refining facilities has delayed a major effort at commercialization. As complements to the research and development efforts of the petroleum industry, the panel recommends that the government support its own program, emphasizing basic and exploratory research.

Fundamental Data Needs for Coal Conversion Technology

(United States Department of Energy, TID-28152,
Revised Edition, January 1981)

This is a comprehensive report prepared by Recon Systems, Inc., of Princeton, New Jersey, for the U.S. Department of Energy. The most important findings are summarized in the abstract:

ABSTRACT

Inaccurate fundamental data used to design plants can affect performance and economics in ways which range from insignificant to critical. Work reported here was formulated both to detect fundamental data needs for coal conversion processes and to assess, as accurately as possible, the absolute and relative importance of those needs.

Research recommendations based on this analysis include additional characterization work on coals, carbonaceous products, and coal ash; extensive characterization of coal-derived liquids and supporting research on pure compounds; experimental and theoretical studies on phase equilibria involving coal-derived liquids and gases, and pure compounds; and miscellaneous engineering studies vital to successful development of coal conversion processes.

Design Properties of Coal Liquids: Edited Workshop Proceedings

(United States Department of Energy, CONF 810381; Workshop held
March 2-4, 1981, at Fountainhead Lodge, Oklahoma.
Proceedings published, August 1981)

These are the edited proceedings of an extensive workshop attended by representatives of industry, universities, and government. Their conclusions are well summarized in the abstract.

ABSTRACT

Over 60 representatives of industry, universities, and government were invited to a 2-1/2-day workshop focusing on the needs for better data on the physical and thermodynamic properties of coal liquids. As a result of the many small group and plenary discussions, the following conclusions were reached.

- o More and better properties data are needed to improve the operational performance of coal liquefaction facilities.
- o Existing, petroleum-based correlations of physical and thermodynamics properties have limited applicability for coal-derived liquids.
- o More and better properties data are needed for designing coal liquids facilities.
- o Several new characterization techniques are applicable, within limits, to heavy distillates and residuum.
- o Better experimental techniques and advanced equipment are needed for characterizing small samples of coal liquids, especially oxygenated compounds, at high temperatures and pressures.
- o Progress in characterizing coal liquids will be hastened by the definition of standard characterization methods and the availability of reference samples for calibration.
- o Data on several types of binary and multicomponent mixtures are essential to the development of properties correlations for coal liquids.
- o Computer modeling and simulation techniques must be improved in parallel with advances in properties data and correlations.
- o Properties research requires long-term commitments, stable funding, specialized laboratories, and highly dedicated scientists.
- o An adequately financed and coordinated effort is needed to prepare pure coal-derived chemicals for use in properties measurements.
- o An expanded research program for properties measurements and correlations has the best prospects for success when there is broad industrial participation.
- o Pilot plants, if utilized effectively, have the potential of yielding much useful design and properties information.
- o Governmental participation would help overcome possible legal and institutional barriers to industrial cooperation in properties research.

Survey of Design Data Needs for Refining Synthetic Crudes

(Bechtel Group Inc. Draft
Final Report, December 1981)

The survey contained in this report was prepared by the Bechtel Corporation under contract to the American Petroleum Institute. We reproduce the summary.

SUMMARY

The information collected in this report on physical property measurements and correlations, data needs, and syncrude refining studies indicates the need for a four-step attack on the problem of design data needs for refining synthetic crudes. The recommendations of this report can be summarized as follows:

1. Contact the firms involved in shale oil, coal liquids, and tar sands development to determine if they are willing to release inspections of syncrudes and syncrude fractions for use in this project.
2. Establish a study to determine how reliable the physical properties need to be for various engineering calculations. This study will establish priorities for the experimental work.
3. Obtain a variety of syncrudes, have them fractionated into suitable cuts, and run comprehensive petroleum inspections on the syncrudes and the fractions. Using the data so obtained together with the data from Step 1, evaluate the existing correlations for characterization. If the existing correlations are inadequate, the data bank can be used to develop new correlations.

A follow-on program requires obtaining experimental flash equilibrium data and enthalpy data for the syncrudes and fractions for checking vapor-liquid equilibrium prediction methods and enthalpy prediction methods.

4. The possibility of product specification revisions to permit better utilization of the aromatic synfuels needs to be investigated.

Fundamental Data Needs for SGN Production

(Report prepared by C. F. Braun and Company
for the Gas Research Institute, July 1982)

The following paragraphs are reproduced from the summary of this report.

The major fundamental data needs were determined by examining each downstream unit for each process. The major data gaps were found in the areas of raw gas and by-product oil characterization, vapor-liquid equilibria (VLE), and effects of minor and trace components on the liquid and gas processing units. The specific needs are outlined below:

Raw Gas Characterization. Expected concentration ranges of minor components (NH_3 , COS, CS_2 , mercaptans, phenols, and oils for example) and trace components (particularly trace metals) are needed to define the needed design methods. For the Lurgi process, methods of predicting properties of by-product oils and tars are needed since many of the methods derived from the petroleum industry do not work for highly aromatic oils. Heating value correlations are particularly needed.

Vapor-Liquid Equilibrium (VLE) Data. VLE data are needed, particularly in the raw gas quench section. Data and theoretical methods are needed at high pressure (600 psig) and high temperature (up to 1800°F) for aqueous electrolyte systems (with CO_2 , NH_3 , H_2S , COS, CS_2 , phenols, fatty acids) in contact with aromatic liquid hydrocarbons. VLE data for trace components that cause catalyst poisoning, such as arsenic compounds, are also needed. New methods need to be developed, using existing methods as a starting point, that will simulate these non-ideal systems.

Miscellaneous. When the feed streams to the gas and liquid processing units are better defined, areas such as catalyst poisoning, minor component solubilities in acid gas removal (AGR), solvents, and metal contamination of saleable sulfur by-products need to be investigated in depth. The effects of oils on catalysts and AGR solvents need to be studied.

Thermophysical Properties for Synthetic Fuels

(Brown University Report, J. Kestin, Editor, November 1982. Report prepared by Working Group on Thermophysical Properties of Synthetic and Related Fuels)

The executive summary of this report is reproduced here.

EXECUTIVE SUMMARY

This report starts with the premise that this country must develop the production of synthetic fuels from coal and shale - eventually. Its purpose is to survey the need for an adequate data base of physico-chemical properties of substances required by the emerging synfuels industry. The report examines the differences which characterize the liquids that occur in the manufacture

of synthetic fuels compared with those that are presently handled by the petroleum industry. The conclusion is that the new requirements constitute more than a simple extension of the scope and ranges of existing data bases.

Having established that there exists a need for the creation of a considerably expanded data base, the report recapitulates the benefits that arise from its availability. The report then examines the standard steps which are conventionally taken to build a computerized data base of thermo-physical properties and enumerates the needed chemical and physical properties of the fluids which occur in the production of synfuels. These are found to be of a scope and range which cannot be covered by utilizing the information available in the existing open literature. The conclusion is that a computerized data base could not be created now and that, therefore, steps should be taken to start creating a reasonable base for it as soon as possible.

The steps which are necessary to take consist of:

- o the development of methods to sample and to characterize samples from process streams
- o the development of improved predictive correlation methods to cope with the increased complexity
- o the creation of a base of carefully performed measurements on pure components and on prepared mixtures (as distinct from cuts) for the validation of correlations
- o the expansion of existing experimental facilities in the country in support of the program of measurements
- o the creation of a mechanism or center for the coordination of activities and to secure a continuous exchange of ideas and methods between industry and academic and government laboratories and between experimentalists, theoreticians, and correlators.

An analysis of the characteristic time needed for an orderly development of a data base in contrast with the characteristic time required to design and construct a plant indicates that work on the former should precede work on the latter by as long a period of time as possible. The same disparity of time scales argues strongly that the Government should assume a major if not leading role in the program under discussion. Except for the creation of a highly visible coordinating center, no essential change in operation through

peer-reviewed unsolicited proposals is recommended. It is, however, suggested that prospective authors of proposals should familiarize themselves with this report before the formulation of their own plan.

Several institutions sponsored reports on the needs of the synfuels industry; the present report differs from them in its emphasis and, most importantly, in that it suggests a possible strategy for the creation of a data base for designers. This strategy may be of use to the program now being developed by the Office of Basic Energy Sciences.

Conference on Coordination of Physical, Chemical and
Thermodynamic Properties of Coal Conversion

(Oak Ridge National Laboratory, June 2-4, 1982, ORNL/TM-8541)

The abstract of this conference report is reproduced here.

ABSTRACT

A Conference on Coordination of Physical, Chemical, and Thermodynamic (PCT) Properties for Coal Conversion was held at Oak Ridge, Tennessee, on June 2-4, 1982. The Conference was provided by the Department of Energy, Oak Ridge Operations (DOE-ORO). To facilitate the workshop format, the Conference attendance was limited by invitation to about 42 participants. The format included: (1) a plenary session with presentations by respected government, industry, and academic leaders, each discussing their role in PCT properties data generation and dissemination, (2) workshops on the topics of data generation, data correlation, and uses of data, and (3) an open discussion to reach consensus viewpoints.

The principal results of the Conference were:

1. Recognition that a centralized data bank of high quality is critical to large-scale coordination of coal conversion work,
2. An agreement that some form of quality assessment of the information to be included in the data bank is necessary,
3. a recommendation to form a "National Steering Committee" with working groups, and
4. a decision to send a letter on behalf of the Conference attendees to Dr. Sun Chun, Director of the Pittsburgh Energy Technology Center (PETC), requesting the organization of a "National Steering Committee."

The Conference organization and the ensuing results are discussed in detail in this report.

Proceedings of the National Science Foundation Workshop
Thermodynamic Needs for the Decade Ahead: Theory and Experiment

(S. I. Sandler, Chairman, October 28-29, 1983,
Washington, DC, two volumes)

The first paragraph of the preface to the report is reproduced here.

This document is the Proceedings of a National Science Foundation sponsored workshop entitled "Thermodynamic Data Needs for the Decade Ahead: Theory and Experiment" held in Washington, DC, on October 28 and 29, 1983. This workshop brought together 33 attendees from universities, industry, and government agencies to identify research needs, goals, and opportunities in chemical engineering thermodynamics. The participants represented a diversity of interests and viewpoints, spanning the range from the traditional chemicals and fuels industries to emerging biochemicals and solid-state processing technologies. The organization and funding of research at universities were also major topics of discussion at this workshop. Indeed, many comments on the methods of funding university research, its stability, and its goals appear in these Proceedings, together with contrasts between research funding in the United States and abroad.

Thermodynamics Research Needs for Fossil Fuels

(Conference at National Institute for Petroleum and Energy Research
November 4-5, 1985)

A summary of the recommendations from the above conference is reproduced here. Most of the recommendations refer to present and possible future research at NIPER.

The thermodynamics research planning meeting was held at NIPER on November 4-5 with attendance by representatives of Exxon, Shell, Phillips Petroleum Company, Amoco Chemicals, and Oak Ridge National Laboratory.

A. Thermochemical Research Needs

1. Continue study of the families of compounds that are presently being studied. Included are polynuclear aromatic hydrocarbons, hydrogenated polynuclear aromatic hydrocarbons, nitrogen compounds, oxygen compounds, and sulfur compounds.
2. The petroleum companies have great interest in the study of amines, phenols, and ethers.
3. The more petrochemical-oriented interests suggest study of alkanolamines, esters, and ketones in addition to the above compounds.
4. A suggestion was made that we check the recommended compound list of DIPPR Committee 801. (Design Institute for Physical Property Data, American Institute of Chemical Engineers.)
5. Extend the temperature range of measurements whenever possible, particularly heat capacity and vapor pressure.
6. Aim the experimental work at key compounds, so that correlations can be built and improved for whole families of compounds.
7. Studies on real process fluids are essentially useless, good only for today. Use such studies only occasionally as checks.
8. Give some thought to publication of results, at least summaries of many papers, in such places as Hydrocarbon Processing and the Journal of the American Institute of Chemical Engineering where working engineers will find them.
9. Concentrate your efforts on your strengths, and the thermochemistry area is an important one.
10. The area is long-term basic research, and the federal government ought to fund it.

B. Research Needs in Thermophysical Properties Measurements

The major problem areas suggested in discussion follow:

1. Handling heavy components, especially in combination with light components.
2. Multiphase systems, especially when water is a component.
3. Heterogeneous systems--in terms of size, chemical types, and polarity.
4. Highly polar and associating systems of components such as acetic acid, formaldehyde, and water.

Concern was expressed about our V-L-E system with its relatively long residence times at high temperature that can cause decomposition.

In addition to the above reports, two on the necessity for data evaluation activities are drawn to the reader's attention. Both reports highlight the importance of thermophysical properties data to technology and the growing importance of the role of the accuracy of the data. The reports are:

National Needs for Critically Evaluated Physical and Chemical Data
(Committee on Data Needs, National Research Council, Washington, DC, 1978)

and

The Technological Importance of Accurate Thermophysical Property Information (edited by J. V. Senger and M. Klein, NBS Special Publication 590)

12. ACTIVE CHEMICAL THERMODYNAMIC LABORATORIES

It is not possible in the time scale for producing this report or, in limiting its content, to list all the laboratories working on chemical thermodynamic property measurements. Anyone requiring such information is referred to the Bulletin of Chemical Thermodynamics (1) which attempts to list thermodynamic laboratories and the work being undertaken therein. The Bulletin covers the world as is customary for a project sponsored by IUPAC (International Union of Pure and Applied Chemistry) and hence is a unique publication for details of work being undertaken in the Eastern Block and the USSR.

This report would, however, like to draw attention to the dwindling number of laboratories within which systematic studies on the measurement of properties leading to Gibbs free energies of organic compounds are being undertaken. Within the United States there appears to be two active groups measuring enthalpies of combustion of organic compounds with the precision required for chemical equilibrium calculations (E. S. Domalski's group at NBS, Gaithersburg, MD, and the group at NIPER). The equipment for such measurements exists at other laboratories in industry, universities, and National Laboratories but does not appear to be in active use. In Europe, inactive equipment is again the general case with the exception being the group headed by G. Pilcher at Manchester, England, who has taken over the apparatus previously used at the National Physical Laboratory, England, which no longer undertakes chemical thermodynamic measurements. Other prominent European groups who measured precise enthalpies of combustion, notably at Lund, Sweden, and the Free University of Amsterdam, are also in decline. In contrast, the East European and USSR groups are very active, notably those headed by Rabinovich at Gorky, Kozina at Moscow State University, and Kolesov also at Moscow State University.

A similar situation exists with laboratories determining absolute entropies and heat capacities. Along with the laboratory at Bartlesville, the only active groups studying organic molecules outside the Eastern Block countries are those of de Knef at Utrecht, Holland; Dworkin, Orsay Cedex, France; and Suga's group at Osaka, Japan. No one using conventional equipment except the Bartlesville group is making measurements above 300 K. Many groups are using differential scanning calorimetry (DSC) to obtain heat capacity

data, but the precision and accuracy of the data is not good with the exception of the results of Mraw at Exxon Research Laboratories. Using specially designed high pressure cells, we have recently obtained results with a precision of ± 1 percent on the DSC over temperature ranges up to the critical point measuring heat capacities. With regard to industry in general, it is known that a large amount of thermodynamic measurements are being accumulated, but its publication record is not good, and it is difficult to know exactly what measurements are being made.

The groups active in thermodynamic measurements other than those mentioned above are numerous. Table 12.1 lists the active groups making thermophysical property measurements in the United States. Time and space precludes a detailed listing for the rest of the world. The Bulletin of Chemical Thermodynamics is a source of further details.

TABLE 12.1 Active groups in thermophysical property measurements
in the United States

Laboratory	Temperature range	Pressure range
<u>Vapor-Liquid Equilibria</u>		
NIPER, Bartlesville	300-700 K	250 bar
University of California, Berkeley	300-500 K	100 bar
Clemson University	65-300 K	150 bar
Colorado School of Mines	200-650 K	140 bar
University of Delaware	300-600 K	400 bar
Kansas University, Lawrence	70-425 K	400 bar
NBS, Gaithersburg,	300-350 K	100 bar
Oklahoma State University	300-530 K	700 bar
Purdue University	300-700 K	250 bar
Rice University	100-700 K	600 bar
Texas A&M University	100-570 K	350 bar
Tulsa University	112-600 K	600 bar
Union Carbide	273-500 K	30 bar
Wilco, Inc.	350-780 K	14,000 bar
Chromaspec, Inc.	300-725 K	125 bar
<u>Pressure-Volume-Temperature</u>		
NIPER, Bartlesville	238-623 K	400 bar
Brigham Young Univiersity	170-670 K	300 bar
Cornell University	70-500 K	10 kbar
Georgia Institute of Technology	300-473 K	400 bar
Los Alamos Scientific Laboratory	4-400 K	100 kbar
NBS, Boulder	14-900 K	800 bar
Notre Dame University	500-650 K	450 bar
Purdue University	300-700 K	300 bar
Rice University, Houston	100-700 K	600 bar
Texas A&M University	90-673 K	200 bar
Wyoming University, Laramie	70-300 K	500 bar
Ohio State University	300-575 K	350 bar
<u>Vapor Pressure</u>		
NIPER, Bartlesville	200-600 K	0.01-3 bar
University of California, Los Angeles	90-320 K	70 bar
Rice University, Houston	100-700 K	100 bar
Texas A&M University	90-475 K	700 bar
Union Carbide, Charleston, W.V.	273-500 K	30 bar
Ohio State University	300-500 K	100 bar

TABLE 12.1 Active groups in thermophysical property measurements
in the United States--continued

Property	Laboratory	Temperature range	Pressure range
<u>Other Thermodynamic Properties</u>			
<u>Speed of Sound</u>	NIPER, Bartlesville	98-573 K	300 bar
	Cornell University	70-500 K	10 kbar
	NBS, Boulder	14-300 K	350 bar
	NBS, Washington, DC		
<u>Enthalpies of Mixing</u>	Brigham Young Univ.	270-470 K	300 bar
	Texas A&M		
	Cornell		
<u>Total Enthalpy</u>	University of Delaware		
	Texas A&M		
	Rice University		
<u>Viscosity</u>	Brigham Young Univ.	170-570 K	300 bar
	Brown University	300-570 K	500 bar
	NBS, Boulder	14-300 K	350 bar
	Oklahoma State Univ.	300-535 K	69 bar
	Rice University	100-650 K	600 bar
<u>Surface Tension</u>	Brigham Young Univ.	170-570 K	300 bar
	Wilco, Inc.	to 500 K	14 kbar
<u>Density</u>	Brigham Young Univ.	170-570 K	300 bar
	Oklahoma State Univ.	300-535 K	69 bar
	Wilco, Inc.	to 500 K	14 kbar
<u>Thermal Conductivity</u>	Brown University	300-420 K	600 bar
	NBS, Boulder	14-300 K	800 bar

References

1. Bulletin of Chemical Thermodynamics, edited by R. D. Freeman. Yearly index, bibliography, and review of published and unpublished research prepared under the auspices of Commission 1.2 on Thermodynamics, IUPAC. Thermochemistry Inc., Stillwater, Oklahoma, USA.